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ATMOSPHERIC DEPOSITION IN THE MUSKOKA-HALIBURTON AREA OF ONTARIO

(1976-1992)

JANUARY 1994

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ATMOSPHERIC DEPOSITION IN THE MUSKOKA-HALIBURTON AREA OF ONTARIO (1976-1992)

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January 1994

PREFACE

The Data Report Series is intended as a readily available source of basic data collected for lakes and watersheds in the Muskoka-Haliburton area of Ontario. These data were collected as part of the Lakeshore Capacity Study and/or the Acid Precipitation in Ontario Study.

The Lakeshore Capacity Study (1975-81) was initiated to investigate the relationships between lakeshore development and lake trophic status in low ionic strength Precambrian Shield lakes. The Acid Precipitation in Ontario Study (1979-present) was initiated, in part, to investigate the effects of the deposition of strong acids on aquatic and terrestrial ecosystems in Ontario. The primary findings of these studies have been and will continue to be published as reviewed papers and technical reports.

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INTRODUCTION

This report summarizes the precipitation data collected in Muskoka-Haliburton from June 1976 to May 1992 as part of the Limnology Section's "calibrated watershed" studies. It includes information on precipitation depth, and concentration and deposition of ions, nutrients and metals.

The appendices include a summary of the annual deposition and concentration time trend plots, and the methodologies employed - both field and analytical - for each chemical parameter.

METHODS

1. Precipitation Collectors

a) Description

The collectors used in this study are bulk collectors and, as such, open all of the time. They collect the wet and at least part of the dry fraction of the deposition.

From September 1976 to May 1978, the collectors were constructed of polyethylene funnels (30 cm diameter) fastened to 250 L plastic containers. The funnels were fitted with 500 μm Nitex mesh to prevent contamination by insects. They were replaced in May 1978 with 0.25 m^2, Teflon-coated, stainless steel funnels. Fiberglass window screening in the funnel opening prevented contamination. The sampling containers were 18 L glass bottles in the summers only. In November 1978, the Teflon funnels were modified with a larger opening for winter sampling using large polyethylene containers (43 cm diameter).

From May 1983, 18 L polyethylene carboys replaced the glass bottles in the summer (Locke and Scott 1986).

b) Site Locations

The number of collectors and their locations changed several times during the study. PT1P (Paint Lake #1) and PT2 (Paint Lake #2) moved with the relocation of the Dorset Research Centre (DRC). PT1P and PT2 moved from the south side (A) of Paint Lake (1976-1977) to the north side (B) of Paint Lake (1977-1980) and, finally, relocated to the present site (C) (1980-92) which is 300 m north of site B (Table 1).

Three sites Carnarvon (CV), Eagle (EG) and Vankoughnet (VT) were removed because of location problems (i.e., near roads). Red Chalk (RC), Crosson (CNP) and Gullfeather (GFP) were removed because of their location resulted in contamination problems. The Harp (HPP) and Plastic (PCP) were on rafts and these were both relocated to land sites in November 1982.

From 1984 to the present, four operated - HYP2, HPP2, PCP2 and PT1P, with a second collector at the Paint Lake site, PT2. These sites also have a Belfort rain gauge, a model 201 RH probe, which measures the hourly and daily relative humidity, temperature (hourly) and daily vapour pressure measurements recorded.

There were minor relocations of the Heney site (HYP2), the Harp site (HPP2) and Plastic (PCP2) to larger clearings.

c) Sampling Interval

The sampling period for the 8 longest term sites ranged from 1 day to 78 days with medians of 2 or 8 days (Table 2). The 78 day period occurred when the lab at Dorset was closed for renovations (October-December 1982). The samples remained in the field during this period.

2. Chemistry

Samples were filtered in the lab to remove coarse particulates either by a 76 μm (1976-1982) or 102 μm (1982-1985) Nitex mesh and 80 μ polyester (Pecap) filter from 1986-1992. A number of changes in sample preservation and chemical analysis occurred during the study (Appendix C). All chemical data were edited by defined criteria (Appendix D).

3. Precipitation Depth

Precipitation depth at each of the sites was measured with either a Standard Rain Gauge (SRG) in summer, or by a Nipher snow collector in winter. The snow collected by the Nipher gauge was melted and depth of water (in mm) recorded. The volume of each sample from each collector was also recorded. The volume data divided by the area of the surface of the collector provided a comparative depth measurement with the Nipher or SRG.

Studies show (Goodison 1978) that Nipher gauges underestimate depth of snow especially during periods of heavy snowfall. The low efficiency of the Nipher gauges is a result of the snow capping the collector. To determine if this happened during this study, data from several Environment Canada weather stations were compared to our data. An estimation technique described by Locke and de Grosbois (1986) used 3-5 Environment Canada stations in the study area with long-term precipitation depth data to determine daily and annual precipitation depths. This model (Meteor) gave a calculation of annual depth data that was compared to our data from June 1976 to May 1986.

4. Calculation of Precipitation Bulk Deposition

The calculation of the daily deposition of each parameter at each site was carried out using Equation 1:

$$\mathrm{Dep} = \frac{C \cdot d}{n} \tag{1}$$

where Dep = daily deposition

C = concentration of the parameter in the sample (Table 3)

d = precipitation depth (mm) at each site

n = the number of days in the collection period

If the reported concentration was "less than" a reported value the reported value was used in the calculation of the daily load.

For each day, an average daily load was generated by averaging the calculated daily loads for each sampling station active at the time. From these, monthly loads were calculated. If there were missing data (i.e., no stations with a valid sample on a given day) the monthly sums were pro-rated if at least 15 days were included in the monthly record.

If there were more than fifteen days of data missing, the monthly load was not reported. The monthly depositions were added to give annual values.

RESULTS

1. Comparison of Precipitation Depth Measurements

A comparison of the daily mean depth as calculated by the estimation technique utilized with Environment Canada data with our measured data demonstrated that our Nipher data under-estimated the depth during the winters of 1976-1977, 1977-1978 and 1981-1982. This inter-comparison (Fig. 2) indicated that our data are underestimates (slope = 0.843). Therefore, during these three winters (also in July 1976 when we collected no data), the monthly depths were derived from Environment Canada stations.

In 1984, three stations (Harp, Plastic and Heney) each had two sites with overlapping collection periods (HPP-HPP2, PCP-PCP2 and HYP-HYP2). The depth measurements at these pairs of sites were very significantly correlated (Fig. 3). All data from all these stations are used in the deposition calculations.

Since the volume of each sample was recorded, an inter-comparison of the measured depth (Standard Rain Gauge (SRG) or Nipher) and a calculated depth (volume of sample ÷ area of the collector) could be made. The comparisons for the eight long term sites (Fig. 4) show a good relationship between the measurements at each site. The scatter in the data at HPP resulted from this site being moved from a raft (August 13, 1976-November 16, 1982) to a land site (November 11, 1982 - present). The inconsistent data are from the raft data subset.

2. Chemistry

The mean annual and range of annual concentrations of each parameter are shown in Table 4 for the 16 years of the study. (The mean annual deposition data (Table 5) is corrected for 3 years (1976-1977, 1977-1978 and 1981-1982) using the combined Environment Canada/MOEE annual precipitation depths.)

The annual summary of the deposition of H^+, SO_4^{2-}, NO_3^- and NH_4^+ (Table 6) and the annual concentration (Table 7) shows the variation during the 16 year study.

The monthly ratio of SO_4^{2-}/NO_3^- (Fig. 5) and NH_4^+/NO_3^- (Fig. 6) based on 192 months of data indicates annual ratio for SO_4^{2-}/NO_3^- as 1.8 and NH_4^+/NO_3^- as 0.73 (Table 8).

DISCUSSION

1. Precipitation Depth

a) Aquatic Science Section and "Meteor"Depth Data

The precipitation depth data are collected at each site by the Aquatic Science Section staff. The "Meteor" data are calculated daily depth using 5 Environment Canada Weather Stations in the Muskoka-Haliburton area (Table 9). The combined data are the best estimate of the annual precipitation depth for 1976-1977, 1977-1978 and 1981-1982 (Table 10).

The combined data using both Aquatic Science Section and "Meteor" monthly values have several problems associated with it. The data collection methods have differences which include:

- The Aquatic Science Section and "Meteor" sites are not in the same location.
- The "Meteor" data (Atmospheric Environment Services sites) are daily data, while the Aquatic Science Section is event data.

- The Aquatic Science Section sites changed several times during the study, while Environment Canada sites did not.

- Most of the Environment Canada snow depth data are daily snow board (depths) (Locke and de Grosbois DR 86/5), which may tend to overestimate the snow depth.

- Spatial problems - i.e., West Guilford receives annually (1191.8 mm) considerably more precipitation than the Muskoka Airport (1009.2 mm) - 30 year means.

- Aquatic Science Section snow depth data are Nipher data which tend to underestimate the snow depth.

b) Aquatic Science Section - Site Location Changes

The Harp (HPP-HPP2), Heney (HYP-HYP2) and Plastic (PCP-PCP2) sites had two sites in operation for a period of time during the study (Table 1). The comparison of depth data for dates when both stations were sampled at each site (Harp, Heney and Plastic), showed strong linear correlations between the two methods (Fig. 3): Harp, $r = 0.990$; Heney, $r = 0.993$ and Plastic, $r = 0.984$. Therefore, the monthly load calculations uses data from both sites during the overlap period.

The comparison of the Aquatic Science Section depth data (mm) and the calculated (volume collected ÷ area of the collector - 0.25 m^2) is linear (Fig. 4). Therefore, the calculated depth was used to fill in any missing depth data.

2. Annual Deposition

The problems of sampling site location (i.e., land and water) and analytical methodology both affect the annual deposition data.

a) Site Location

i) Land

Three land sites including Eagle (EG), Carnarvon (CV) and Vankoughnet (VT) have data problems because of extraneous anthropogenic inputs.

The Eagle Lake site was near the highway, 2 km west of Eagle Lake, and under a high tension hydro line. The Vankoughnet site was at the junction of two roads - Highway 118 and the Clear Lake Road and the Carnarvon site was also near a road - Haliburton County Road #11 (0.5 km west of Highway 118). These sites were removed (CV in 1979 and EG and VT in 1980). In analyzing the data, several samples were removed from the data set for various parameters (P, N, Al and Cl) because of these anthropogenic inputs.

To determine the affect on the monthly depositions, the loads were calculated with each of the three sites removed. The chemical parameters recalculated include: Al, Ca, Cl, DOC, Fe, K. Mg, Mn, Na, NH_4^+, NO_3^-, TKN and SO_4^{2-}.

In 1976-1977, data are missing, therefore, a monthly comparison is not possible, but in 1977-1978 the changes were 3-8%. During 1976-1977 and 1977-1978 all sites are included in the monthly and annual deposition calculations.

ii) Raft

Several of the bulk precipitation collectors were located on rafts including Gullfeather (GFP), Crosson (CNP), Harp (HPP), Plastic (PCP) and Red Chalk (RC). The data collection from these sites were especially difficult during the fall freeze-up and spring melt when the sample periods were from 4-8 weeks. Fecal contamination from birds was common in the samples from these raft sites. Also, the raft locations (usually located in the middle of the lake) had the problem of wind, which reduced collector efficiency. The depth and volume of the samples from the rafts was inconsistent with other land locations. The comparison of the volume collected and depth data (Fig. 4) for HPP (Harp Lake) illustrates the inconsistency caused by the raft location.

The Gullfeather, Crosson and Red Chalk raft sites were eliminated while the Harp and Plastic sites were relocated to land sites (Table 1).

3. Analytical Methodology Changes and Its Effect on Annual Deposition

Annual deposition changes (Appendix A) for several chemical parameters are explained by improvements to the analytical methods (for details for each parameter, see Appendix C).

Cations - Na, Ca, Mg, K

In May 1979, cation analyses moved from the Water Quality Rivers Lab to the Precipitation Lab with a resultant increase in the detection limit for the cations (Appendix C, Tables C15 (Na), C3 (Ca), C9 (Mg), C12 (K).

The analytical improvement resulted in an apparent decrease in mean annual concentration - sodium (83%), calcium (59%), magnesium (59%) and potassium (59%) (Table 11). The data ranges compared are 1976-1979 and 1979-1992.

Chloride

The chloride analyses from 1976 to March 1978 were a colourimetric method in the

Water Quality Rivers Lab. In April 1978, the Precipitation Lab began and the method changed to ion chromatography (Appendix B, Table C4). An improvement to the analytical detection limit (0.03) and range (0-2 mg/L^{-1}) occurred in April 1978.

These improvements resulted in a 52% decrease in the mean annual chloride concentrations (Table 11).

Iron (Fe)

In October 1979, the analysis of iron (Fe) in the precipitation changed from the Water Quality Lab to the Precipitation Lab. An analytical method change occurred in June 1982 from a colourimetric technique to an inductively coupled plasma technique using argon with the analysis by atomic emission spectrophotometry (Table C8, Appendix C). The resultant improvement in the detection limit produced an apparent decrease of 52% (1976-1980 to 1980-1982) and a further reduction of 20% in 1982-1992 (Table 11).

Phosphorus

Between 1976-1979 and 1979-1992, changes in analytical methodology (Appendix C, Table C13), the removal of several sites near roads (CV, EG, VT) and on rafts (RC, CNP, GFP) the relocation of HPP to a land site all contributed to a reduction of the mean annual total phosphorus concentration from 2.55 μmoles $\cdot L^{-1}$ to 0.40 μmoles $\cdot L^{-1}$.

In 1983-1984 an increase in deposition occurred (0.88 m moles $m^{-2}yr^{-1}$) because of a major storm on May 2, 1984. This sampling period (May 1984) dominates the phosphorus deposition for the year (1983-1984). The storm contributed 28.5% of the annual total.

Aluminum

The analytical methodology changes are numerous for aluminum through the study (Appendix C, Table C1,). The mean annual concentration data ranges from 4.19 μmoles $\cdot L^{-1}$ to 0.34 μmoles $\cdot L^{-1}$. The high aluminum data similar to phosphorus results from the poor site locations (i.e., road dust and fecal contamination).

Silicates

The analytical methodology did not change during the study (Appendix C, Table C14). The mean annual concentration is 1.18 μmoles $\cdot L^{-1}$ (range 3.62 - 0 μmoles $\cdot L^{-1}$). Similar to phosphorus and aluminum, the field contamination explains many of the higher data values from 1976-1978. The increase in 1983-1984 results from the major dust storm on May 2, 1984.

SO_4^{2-}

The major method changes occurred in April 1978 (Appendix C, Table C16). The major changes were that a) the analytical lab moved from the Water Quality Lab to the Precipitation Lab, and b) the method changes from a colourimetric technique to ion chromatography.

SO_4^{2-} emissions in eastern North America (Dillon et al. 1988) have declined from 1976 to 1981, but have been approximately constant since 1982, and so a comparison of the first 5 years of data (1976-1977 to 1980-1981) with the last 11 years (1982-1983 to 1991-1992) is made.

The average SO_4^{2-} concentration (Table 6) in the early period (78.3 μeqL^{-1}) was 28% higher than that in the latter (56.2 μeqL^{-1}). The drop in SO_4^{2-} deposition was similar (30% from 80.9 to 56.6 meq $m^{-2}yr^{-1}$) (Table 7) as a result of the fact that, on average, the amount of precipitation was only slightly (5%) different between the two periods.

Hydrogen Ion

The pH measurement had only one minor analytical method change. From June 1982 to the end of the study, the initial pH reading for the Gran alkalinity analyses was the reported pH value. Before June 1982, the pH reading was analyzed separately on a Radiometer pH meter (Appendix C, Table C7). (This change did not produce any significant differences with the pH data.)

The H^+ concentration changes closely followed the SO_4^{2-} concentration changes, dropping from 77.8 to 55.7 meq L^{-1}, a decrease (28%) almost identical to that of SO_4^{2-} concentration.

Nitrate and Ammonium

Several changes occurred during the study in both field and analytical procedure for nitrate and ammonium (Appendix C, Tables C11 (nitrate) and C2 (ammonium)).

The average NO_3 concentration from 1976-1981 was 40.8 μeq L^{-1}, slightly higher than the average (37.9 μeq L^{-1}) for the last 11 years (1982-1992). The deposition rates (42.4 and 37.7 meq $m^{-2}yr^{-1}$) were also, as for SO_4^{2-}, similar. Thus, there is no indication that the NO_3^- levels measured in the deposition have increased; in fact, a slight decrease is apparent.

The average NH_4^+ concentration from 1976-1981 was 30.5 μeq L^{-1}, higher than the average (25.1 μeq L^{-1}) for the last 11 years (1982-1992. The deposition rates decreased (31.7 to 24.9 meq $m^{-2}yr^{-1}$).

CONCLUSIONS

Between 1976-1990, a series of 14 collector sites in the Muskoka-Haliburton region measured volume and concentration in the bulk precipitation.

In summary:

1. The Muskoka-Haliburton mean annual precipitation depth averaged 1015.4 (n=16) mm and ranged from 899.0 (1991-1992) to 1230.3 (1982-1983).
2. A decrease in annual deposition of H^+, SO_4^{2-}, NO_3^- (also see Dillon, Lusis, Reid and Yap 1988).
3. The decrease in annual mean concentration data for many parameters is related to improved chemical methodology and removal of sampling locations from sources of contamination.
4. The chemical analytical history is vital for data interpretation.
5. For the 8 long-term collectors, an excellent relationship existed between depth and total volume of precipitation measured.
6. The SO_4^{2-}/NO_3^- ratio decreased during the 16 year study and, although NO_3^- concentration did not increase, it is becoming relatively more important to the anion content of the precipitation.

ACKNOWLEDGEMENTS

The precipitation network in the Muskoka-Haliburton area is funded by the Ministry of Environment and Energy through the Lakeshore Capacity Study (1976-80) and the Acid Precipitation in Ontario Study (1980-92). We wish to acknowledge the contributions of Aquatic Science Section staff, especially Lem Scott, Bob Girard and Barb Hutchinson and the Ontario Ministry of Environment and Energy Laboratory, especially Charles Chun, Don Evans and Peter Sutey and the Air Resources Branch, especially J.P. Varto.

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Table 1 Precipitation station network used by the Dorset Research Centre.

Precipitation Station		**Gauge Codes***	**Dates**
CNP	Crosson raft	0, 1, 9, 62	80/05/08 - 82/05/31
CV	Carnarvon	0, 1, 9, 61, 62	76/08/16 - 79/01/24
EG	Eagle	0, 1, 9, 61, 62	76/08/17 - 80/05/02
GFP	Gullfeather raft	0, 9, 62	76/07/30 - 78/11/08
HPP	Harp raft	0, 1, 9, 61, 62	76/08/13 - 82/11/16
HPP	Harp 3A	0, 1, 62	82/11/16 - 84/05/02
HPP2	Harp 4	3, 62	84/01/17 - present
HYP	Heney west	0, 1, 62	82/11/16 - 84/10/30
HYP2	Heney east	3, 62	84/01/10 - present
PCP	Plastic raft	0, 1, 9, 62	80/05/02 - 82/11/16
PCP	Plastic gravel pit	0, 1, 62	82/11/18 - 84/10/30
PCP2	Plastic north shore	3, 62	84/01/17 - present
A-PT1P	Dorset site (Paint)	0, 1, 61, 62	76/11/09 - 79/11/30
PT2	Dorset (Paint)	62	79/05/04 - 79/11/30
B-PT1P	Dorset site (Micro)	0, 1, 9, 61, 62	79/11/30 - 82/11/16
PT2	Dorset (Micro)	62	79/11/30 - 82/11/16
C-PT1P	Dorset site (Bellwood)	0, 1, 9, 62	82/11/17 - present
PT2	Dorset (Bellwood)	62	82/11/17 - 84/05/02
RC	Red Chalk raft	0, 1, 9, 62	76/08/03 - 78/11/02
VT	Vankoughnet	0, 1, 9, 61, 62	76/05/05 - 80/05 08

*Gauge Codes (Nicolls et al. DRC 86/2)

0	Standard 10 cm rain gauge
1	Nipher snow gauge
3	Belfort rain gauge (also model 201 RH probe - hourly and daily relative humidity, temperature, daily vapourization pressure)
4	Snow rule
9	Volume calculated from bucket (quality control flag)
61	Wet only collector
62	2500 cm^2 square bulk collector

Table 2 Sampling Intervals for the 8 long term precipitation collectors.

	Mean	Median (days)	Maximum	Minimum
HPP	11.7	8	78[1]	1
HPP2	9.2	7	34	1
HYP	9.3	7	28	2
HYP2	9.3	7	49	1
PCP	10.2	7	76[1]	1
PCP2	9.1	7	35	1
PT1P	10.5	8	78[1]	1
PT2	10.9	8	78[1]	1

[1] Chemistry lab shut down for renovations.

Table 3 Parameter description and transformation factors.

1[a]	2	3	4	5	6	7	8
Aluminum	ALUT	Al	0	1	26.98	+2	1
Calcium	CAUR	Ca	2	1E3	40.08	+2	1E3
Chloride	CLIDUR	Cl	2	1E3	35.46	-1	1E3
Dissolved Organic Carbon	DOC	DOC	2	1E3	12.01	0	1E3
Iron	FEUT	Fe	0	1	55.85	+2	1
Hydrogen Ion	HHI	H	3	1E3	1.008	+1	1E3
Potassium	KKUR	K	2	1E3	39.1	+1	1E3
Magnesium	MGUR	Mg	2	1E3	24.32	+2	1E3
Manganese	MNUT	Mn	0	1	54.94	+2	1
Sodium	NAUR	Na	2	1E3	22.99	+1	1E3
Ammonium as N	NNHTFR	NH$_4$	0	1	14.01	+1	1
Nitrate and Nitrite as N	NNOTFR	NO$_3$	0	1	14.01	-1	1
Total Kjeldahl Nitrogen	NNTKUR	TKN	0	1	14.01	0	1
Precip Depth	pdpth	pdp	0	-3	0	0	0
pH	pH	pH	2	-1	1.008	+1	1
Total Phosphorus	PPUT	TP	2	1	30.98	0	1
Silicates	SIO3UR	Si	2	1	28.09	0	1E3
Sulphate as SO$_4$	SSO4UR	SO$_4$	1	1E3	96.07	-2	1E3

1[a] parameter description
2 LIS parameter name (if upper case)
3 4-character parameter abbreviation
4 # decimals for printing
5 Transformation number, unit code (also, originally used as multiplication factor to convert to μg/L from original input units - now input units are as same output) or unit code:

1E3 = mg/L
1 = μg/L
0 = undefined
-1 = element [conc]/h = 10 (- result)
-2 = metres
-3 = mm
-4 = deg. C
-5 = mL
-6 = moles/L
-7 = μg/L

6 division factor to convert to μg - atom/L
7 charge
8 division factor to convert to output units (after converted to μg/L)

Table 4 Mean annual (June 1 - May 31) concentration for Muskoka-Haliburton bulk precipitation.

		n	Mean	Range	
				Max	Min
Al	μmoles L^{-1}	16	1.16	4.19	0.34
Ca	μequ L^{-1}	16	17.5	38.52	10.81
Cl	μequ L^{-1}	16	5.13	10.44	3.48
DOC	μmoles L^{-1}	14	90.9	223.74	45.45
Fe	μmoles L^{-1}	10	1.11	2.74	0.52
F	μequ L^{-1}	10	0.24	0.37	0.05
H+	μequ L^{-1}	16	62.8	95.64	48.16
K	μequ L^{-1}	16	2.37	7.39	1.26
Mg	μequ L^{-1}	16	4.94	12.21	2.87
Mn	μequ L^{-1}	10	0.104	0.21	0.06
Na	μequ L^{-1}	16	5.69	23.43	2.13
NH_4	μequ L^{-1}	16	26.65	37.01	20.87
NO_3	μequ L^{-1}	16	38.67	45.85	29.77
TKN	μmoles L^{-1}	16	39.14	66.32	28.38
PPUT	μmoles L^{-1}	16	0.77	2.58	0.40
Si	μmoles L^{-1}	16	1.18	3.62	0
SO_4	μequ L^{-1}	16	63.14	88.33	49.01

Table 5 Mean annual (June 1 - May 31) deposition for Muskoka-Haliburton bulk precipitation.

				Range	
		n	Mean	Max	Min
Depth		16	1015.4	1230.3	899.0
Al	mmoles m^{-2}yr^{-1}	16	1.18	3.93	0.30
Ca	meq m^{-2}yr^{-1}	16	17.7	37.71	10.4
Cl	meq m^{-2}yr^{-1}	16	5.18	10.32	3.46
DOC	mmoles m^{-2}yr^{-1}	14	92.8	235.34	55.92
Fe	mmoles m^{-2}yr^{-1}	14	1.12	2.57	0.47
F	meq m^{-2}yr^{-1}	10	0.24	0.35	0.06
H+	meq m^{-2}yr^{-1}	16	64.1	100.60	43.59
K	meq m^{-2}yr^{-1}	16	2.37	6.92	1.35
Mg	meq m^{-2}yr^{-1}	16	4.97	11.44	3.38
Mn	mmoles m^{-2}yr^{-1}	16	0.105	0.20	0.06
Na	meq m^{-2}yr^{-1}	16	5.75	24.13	2.04
NH_4	meq m^{-2}yr^{-1}	16	27.0	38.93	22.31
NO_3	meq m^{-2}yr^{-1}	16	39.1	47.2	33.69
TKN	mmoles m^{-2}yr^{-1}	16	39.6	69.8	30.4
PPUT	mmoles m^{-2}yr^{-1}	16	0.77	2.42	0.36
Si	mmoles m^{-2}yr^{-1}	16	1.21	3.73	0
SO_4	meq m^{-2}yr^{-1}	16	64.2	87.37	46.48

Table 6 Annual deposition of H^+, SO_4^{2-}, NO_3^- and NH_4^+

Hydrologic Year	H^+	SO_4^{2-} ($meq\ m^{-2}$)	NO_3^-	NH_4^+
1976 - 1977	65.30	82.75	35.12	24.24
1977 - 1978	81.53	87.37	43.64	32.26
1978 - 1979	100.60	83.74	42.45	38.93
1979 - 1980	85.40	76.73	47.20	29.98
1980 - 1981	71.46	73.96	42.17	32.23
1981 - 1982	79.27	75.76	40.81	27.06
1982 - 1983	74.53	68.27	36.62	25.68
1983 - 1984	54.00	54.41	36.55	22.31
1984 - 1985	55.72	57.38	36.69	24.98
1985 - 1986	62.07	61.51	41.39	24.18
1986 - 1987	46.22	47.04	33.69	26.23
1987 - 1988	52.23	57.13	42.97	27.55
1988 - 1989	50.26	51.24	34.29	22.42
1989 - 1990	43.59	46.48	37.10	24.18
1990 - 1991	57.68	53.25	39.25	24.82
1991 - 1992	47.23	49.98	36.14	24.89
Mean	64.1	64.2	39.1	27.0
Max	100.6	87.4	47.2	22.3
Min	43.6	46.5	33.7	38.9

Table 7 Annual concentration for H^+, SO_4^{2-}, NO_3^- and NH_4^+ (all the data corrected for precipitation depth).

Hydrologic Year	**H^+**	**SO_4^{2-} (meq m^{-2})**	**NO_3^-**	**NH_4^+**
1976 - 1977	69.67	88.29	37.71	26.03
1977 - 1978	79.17	84.84	42.65	31.53
1978 - 1979	95.64	79.61	40.61	37.25
1979 - 1980	77.73	69.84	43.24	27.46
1980 - 1981	66.68	69.01	39.60	30.27
1981 - 1982	78.29	74.82	40.57	26.90
1982 - 1983	60.58	55.49	29.96	21.01
1983 - 1984	54.44	54.85	37.09	22.64
1984 - 1985	51.80	53.35	34.33	23.38
1985 - 1986	57.79	57.27	38.82	22.71
1986 - 1987	48.16	49.01	35.10	27.33
1987 - 1988	55.73	60.96	45.85	29.4
1988 - 1989	52.26	53.28	35.66	23.32
1989 - 1990	48.46	51.67	41.25	26.88
1990 - 1991	57.68	52.36	38.6	24.42
1991 - 1992	47.23	55.15	40.2	27.69
Mean	62.8	63.14	38.67	26.65
Max	95.64	88.33	45.85	37.01
Min	48.16	49.01	29.77	20.87

Table 8 The annual ratio for SO_4^{2-}/NO_3^- NH_4^+/NO_3^-

	SO_4^{2-}/NO_3^-	NH_4^+/NO_3^-	n
Mean	1.77	0.73	16
Summer Maximum	4.05 (1976-1977)	1.72 (1978-1979)	14
Summer Mean	3.12	1.23	
Winter Minimum	0.31	0.22 (1984-1985)	14
Winter Mean	0.80	0.36	

Table 9 Annual long-term precipitation depth comparison - Aquatic Science Section, "Meteor" and AES (long-term database).

Method of Collection	**No. of Years**	**Annual Mean**	**Stations Included**
Limnology Unit[1]	(10) 8	982.6	Table 10
Combined	8	1052.9	Table 10
Meteor-1	8	1136.9	Dorset, West Guilford, Dwight, Huntsville, Minden
Meteor-2[2]	8	1093.8	Dorset, Beatrice, Huntsville, Dwight, Minden
AES-1[2]	30	1099.4	Dorset, Beatrice, Huntsville, Dwight, West Guilford (1191.0)[3]
AES-2[2]	30	1084.4	Dorset, Beatrice, Huntsville, Dwight, West Guilford, Muskoka Airport (1009.2)[3]

[1] See Table 1 for details

[2] Atmospheric Environment Services (AES) , Environment Canada, long-term weather data from stations in the study area

[3] 30 year Environment Canada Annual mean

Table 10 Annual comparison of precipitation depth for the Aquatic Science Section data, "Meteor" and a combined depth total.

Hydrologic Year	**DRC (1)**	**Meteor (2)**	**Combined Data (3)**	**% (1)/(2) x 100**
1976 - 1977	711.8	942.7	937.3	75.5
1977 - 1978	833.7	1010.99	1029.3	82.5
1978 - 1979	1051.9	1169.25	1051.9	90.0
1979 - 1980	1098.6	1150.7	1098.6	95.5
1980 - 1981	1071.7	1233.5	1071.7	86.9
1981 - 1982	870.5	1103.6	1012.5	78.8
1982 - 1983	1230.3	1321.7	1230.3	93.1
1983 - 1984	991.96	1162.2	991.96	85.3
1984 - 1985	1075.59	1131.0	1075.59	94.6
1985 - 1986	1074.13	--	1074.13	--
8 year average				
1976 - 1984	982.6	1136.9	1052.9	

(1) DRC - data collected from fourteen (14) collectors in various locations in the Muskoka-Haliburton area (1976 - 1986) (Table 1).

(2) Meteor - Meteorological data collected from AES sites in the area including several types of Weather Stations. The annual depth is an average of 5 stations in the study area (Table 9).

(3) Combined - in the winters of 1976 - 1977, 1977 - 1978, few snow depth measurements were made. Therefore, during the winter months data from Meteor is added. In 1981 - 1982, Niphers were in place but because of the sampling period, the data is suspect.

Table 11 Analytical improvements resulting in apparent decreases in annual deposition (Na, Ca, Mg, K, Cl and Fe)

Parameter	**Time Period**	**Mean ($\mu g/L$)**	**% Change**
Na	1976 - 1979	397.72	
	1979 - 1990	65.8	83
Ca	1976 - 1979	673.14	
	1979 - 1990	275.75	52
Mg	1976 - 1979	113.6	
	1979 - 1990	46.7	57
K	1976 - 1979	178.6	
	1979 - 1990	72.7	59
Cl	1976 - 1979	311.5	
	1979 - 1990	150.1	52
Fe	1976 - 1980	127.2	
	1980 - 1982	61.4	52
	1982 - 1990	36.9	20

Fig. 1 A location map of the Muskoka-Haliburton study sites

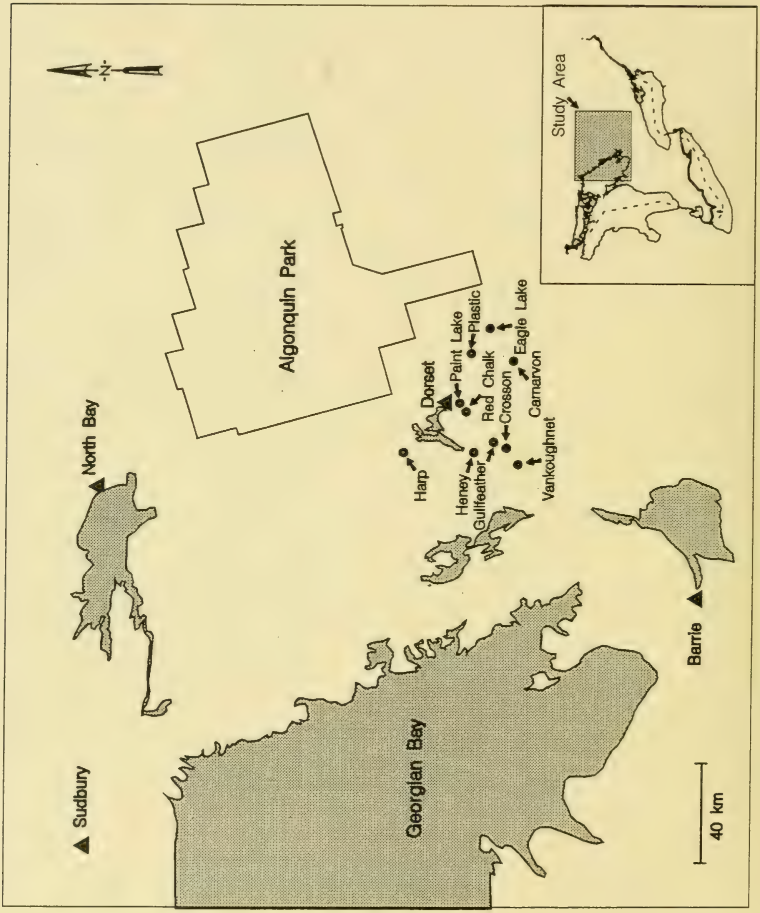


Fig. 2 A comparison of the precipitation depth collected at the fourteen sites with a depth calculated from the Meteorological Data Base (Meteor)

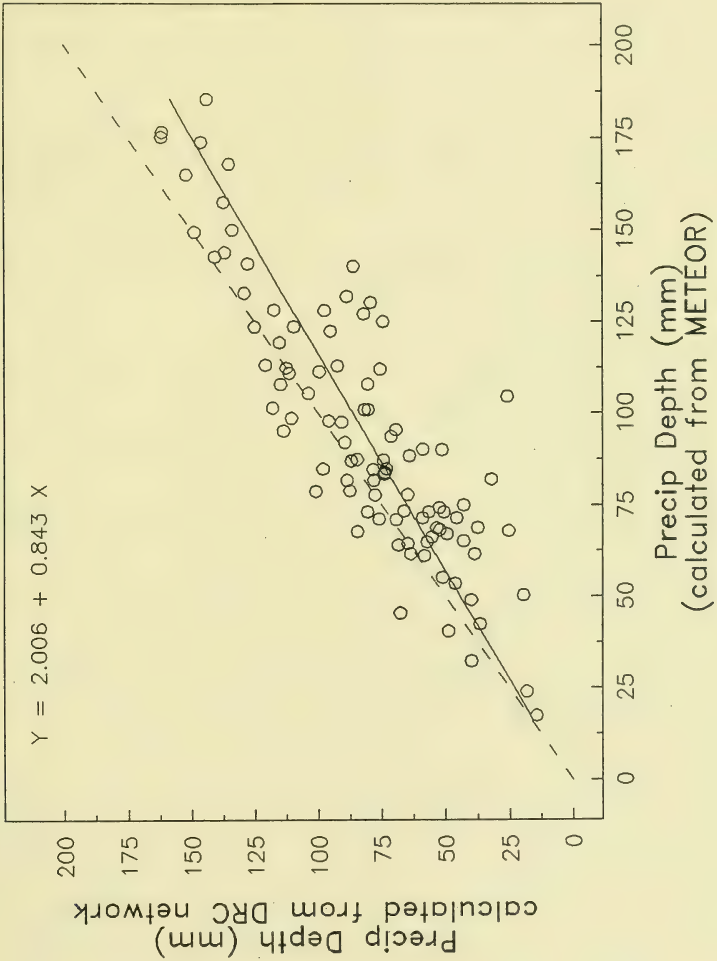


Fig. 3 A depth comparison of HPP-HPP2, HYP-HYP2 and PCP-PCP2

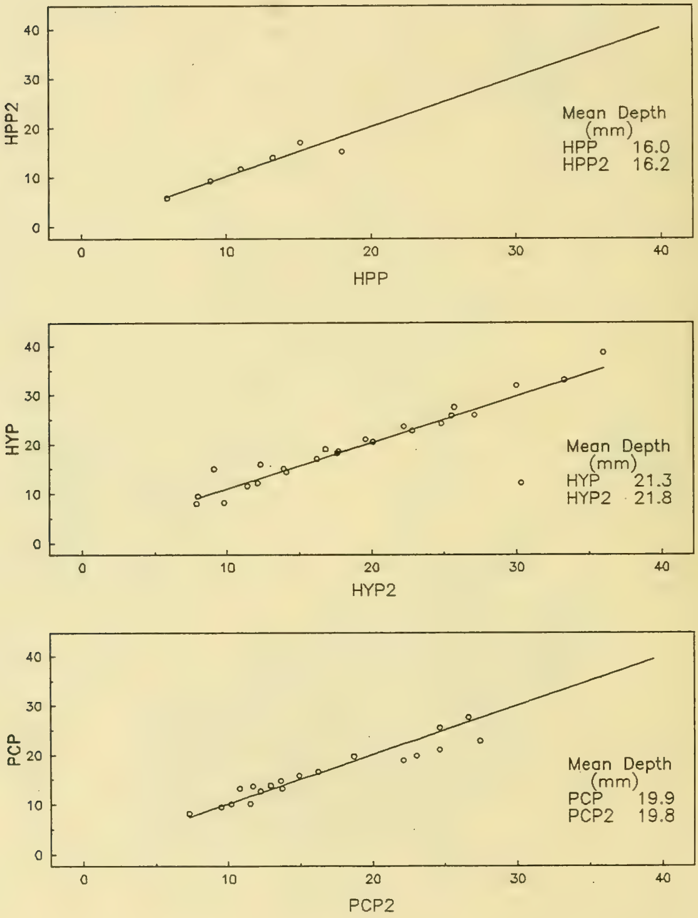


Fig. 4 The relationship between measured precipitation depth and areal adjusted sample volumes

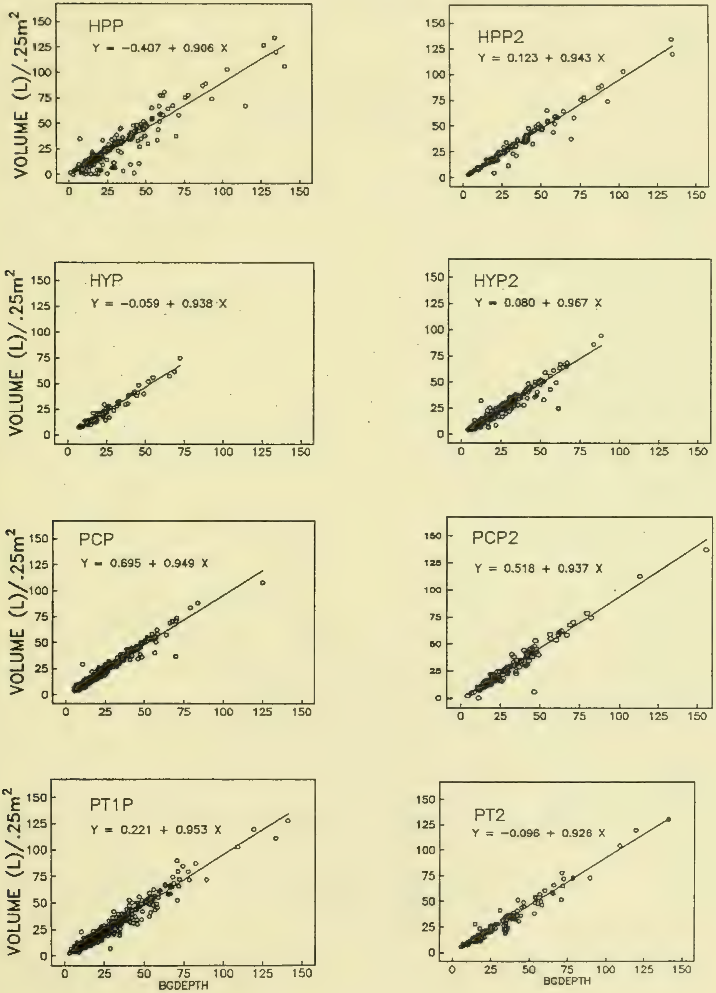


Fig. 5 The ratio of SO_4^{2-}/NO_3^- monthly deposition for the Muskoka-Haliburton bulk precipitation from 1976-1992.

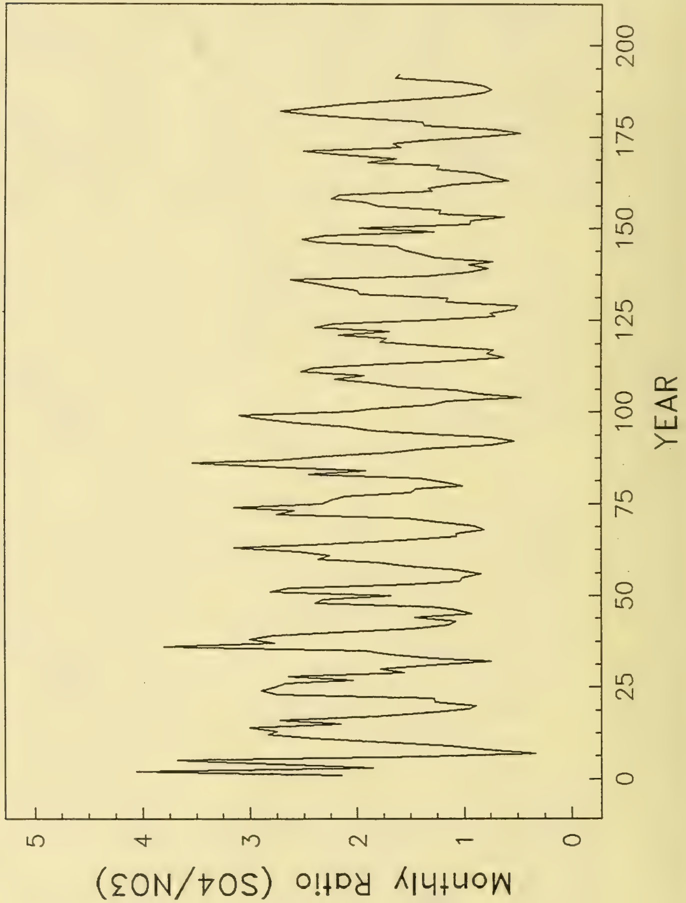
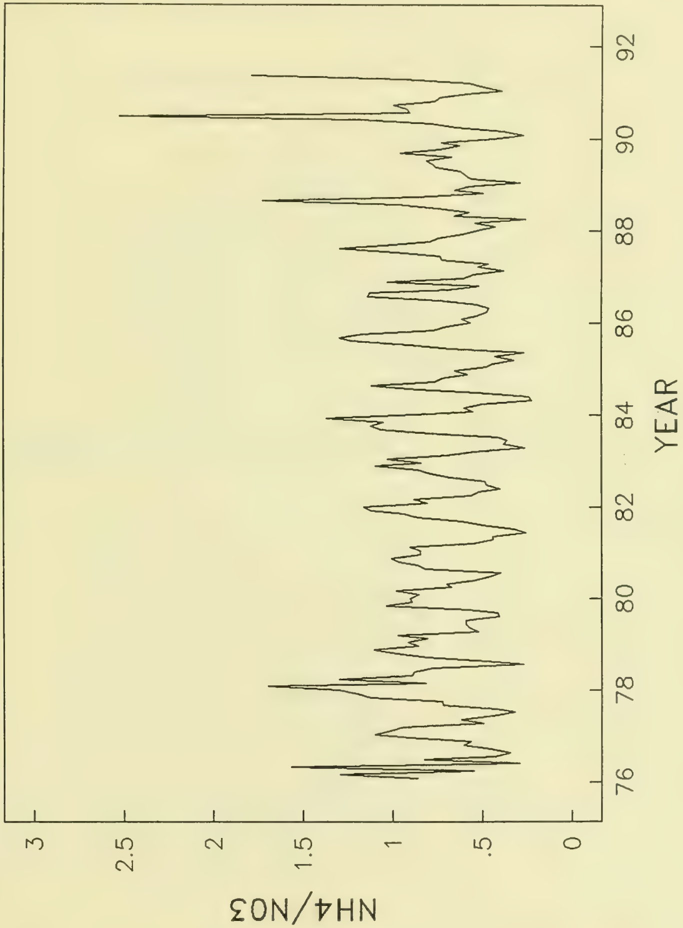


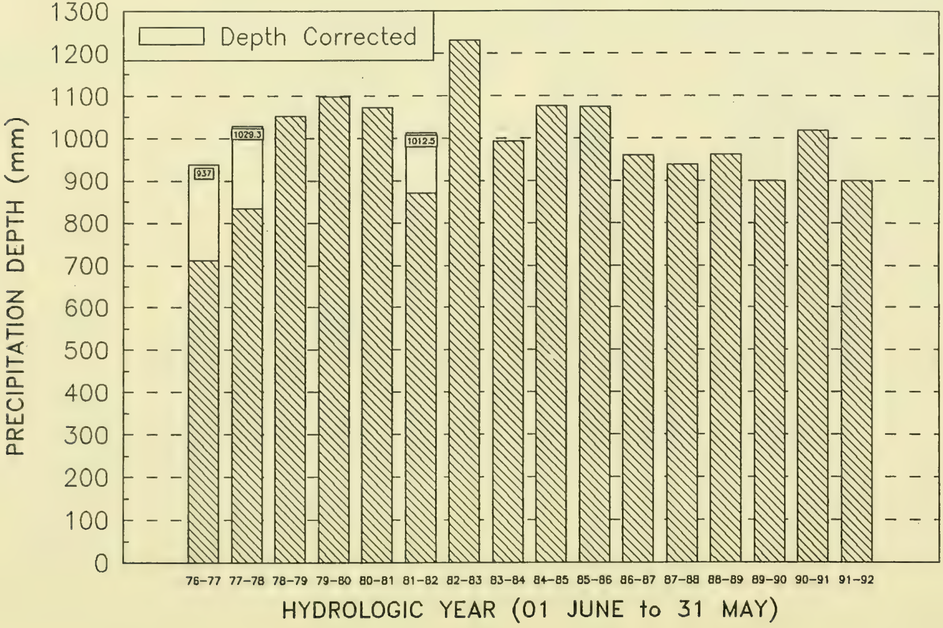
Fig. 6 The monthly ratio of NH_4^+/NO_3^- deposition for Muskoka-Haliburton bulk precipitation from 1976-1992.



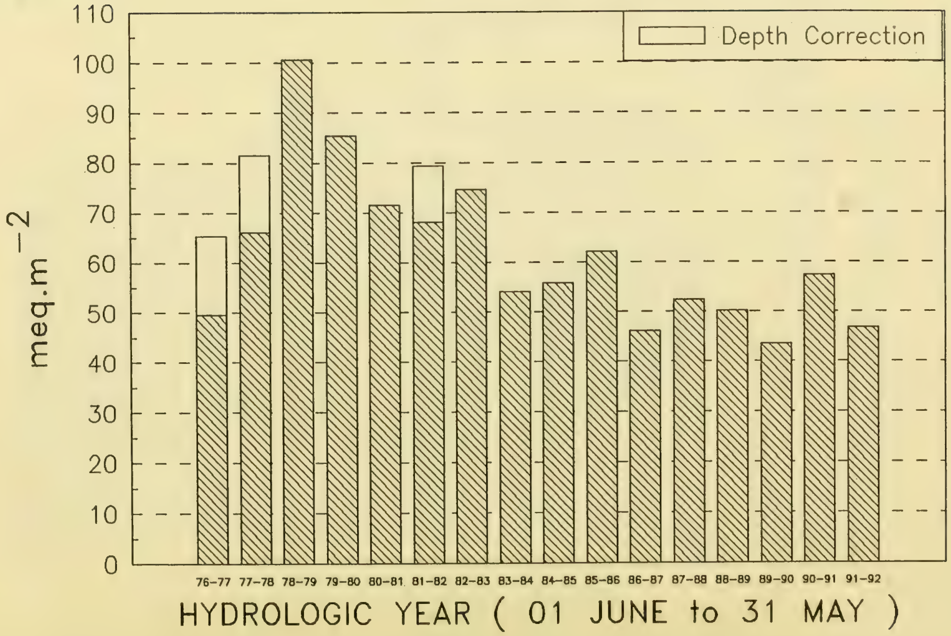
APPENDIX A

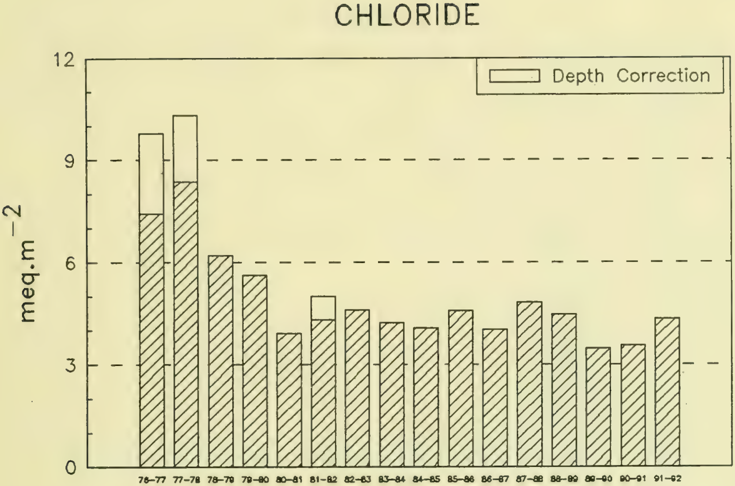
Annual Precipitation Deposition

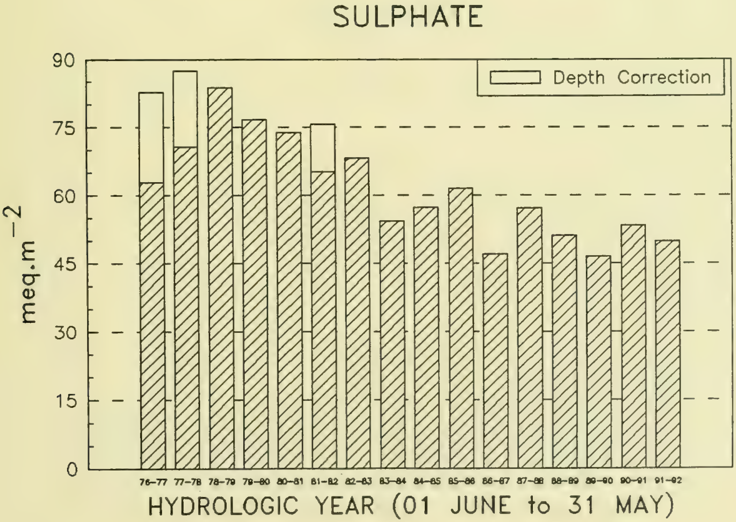
A1 Precipitation Depth
A2 Hydrogen Ion
A3 Chloride and Sulphate
A4 Sodium and Potassium
A5 Calcium and Magnesium
A6 Ammonia and Nitrate
A7 Phosphorus and TKN
A8 Iron and Manganese
A9 Silicate and Aluminum
A10 Dissolved Organic Carbon and Fluoride


Depth Corrected
PRECIPITATION DEPTH (mm)
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
937
1029.3
1012.5
76-77
77-78
78-79
79-80
80-81
81-82
82-83
83-84
84-85
85-86
86-87
87-88
88-89
89-90
90-91
91-92
HYDROLOGIC YEAR (01 JUNE to 31 MAY)

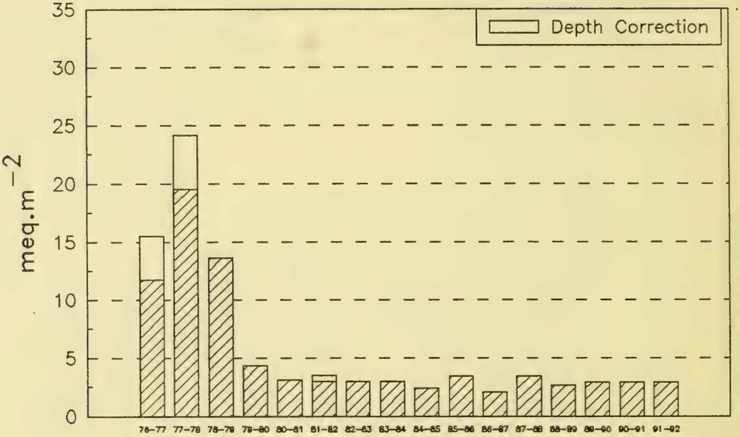
HYDROGEN ION



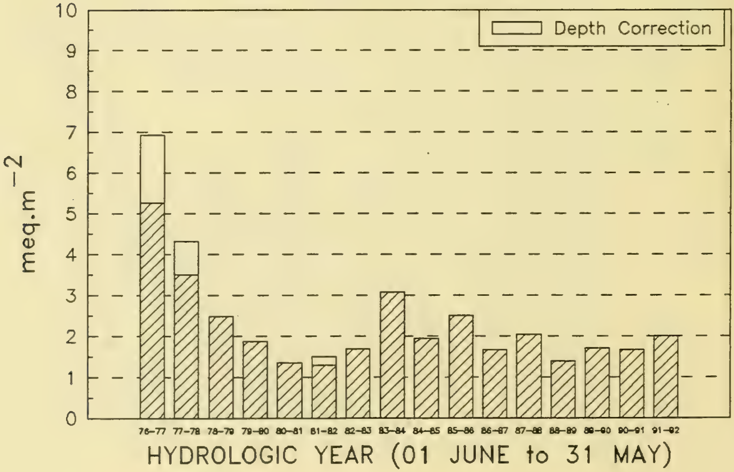

CHLORIDE
Depth Correction
meq.m $^{-2}$
0
3
6
9
12
76-77
77-78
78-79
79-80
80-81
81-82
82-83
83-84
84-85
85-86
86-87
87-88
88-89
89-90
90-91
91-92

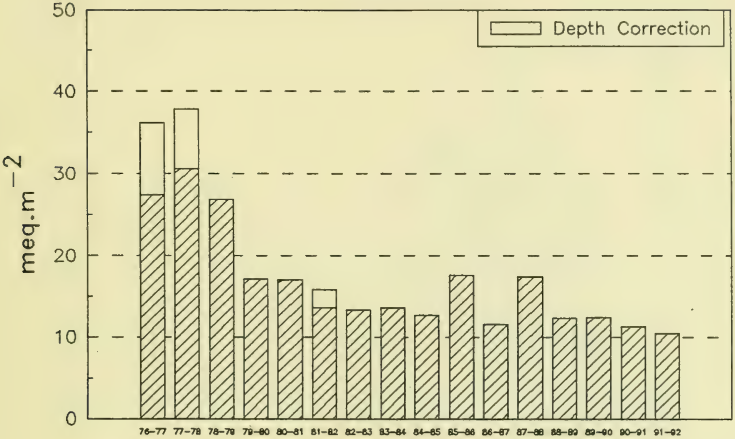

SULPHATE
Depth Correction
meq.m $^{-2}$
0
15
30
45
60
75
90
76-77
77-78
78-79
79-80
80-81
81-82
82-83
83-84
84-85
85-86
86-87
87-88
88-89
89-90
90-91
91-92
HYDROLOGIC YEAR (01 JUNE to 31 MAY)

SODIUM

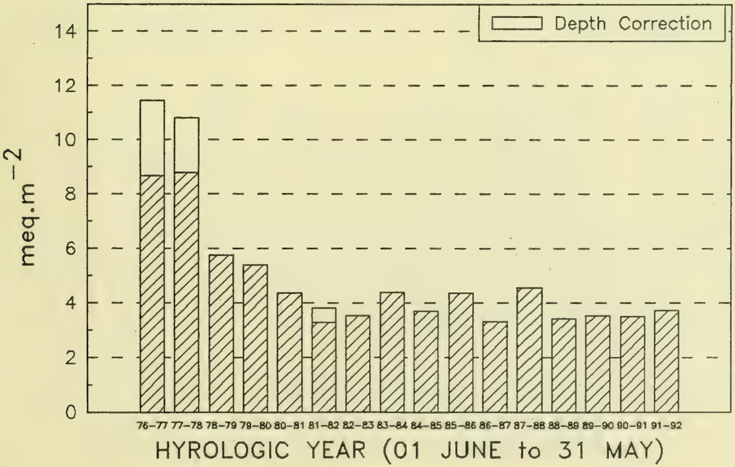


POTASSIUM

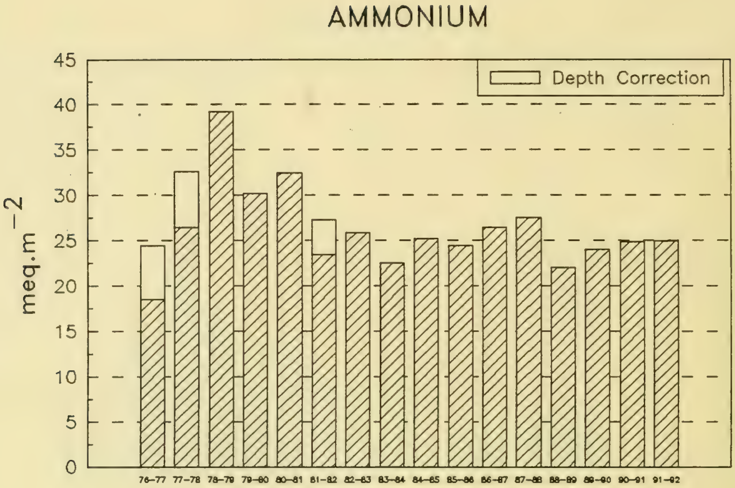




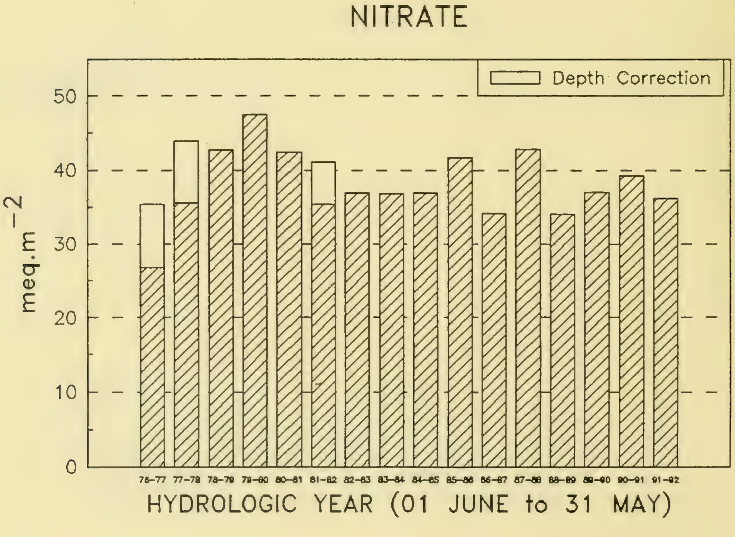
CALCIUM



MAGNESIUM

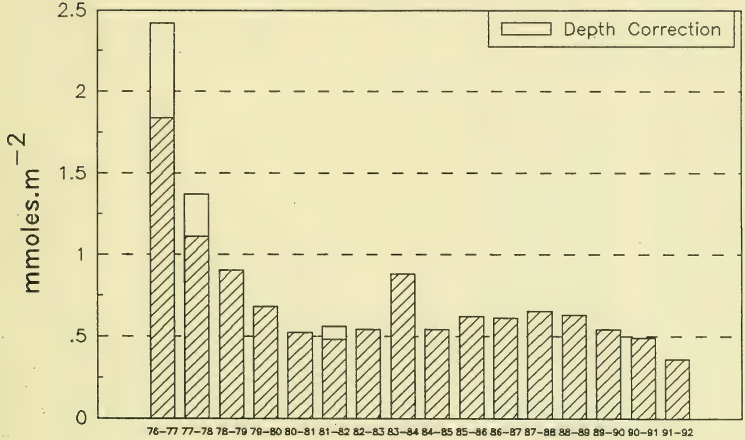


AMMONIUM

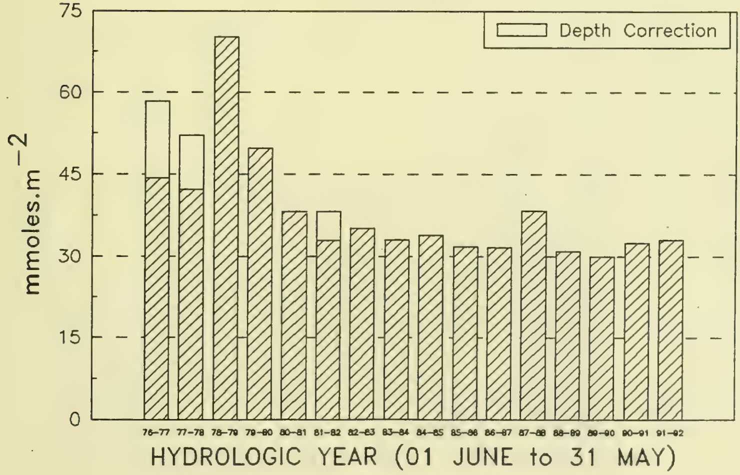


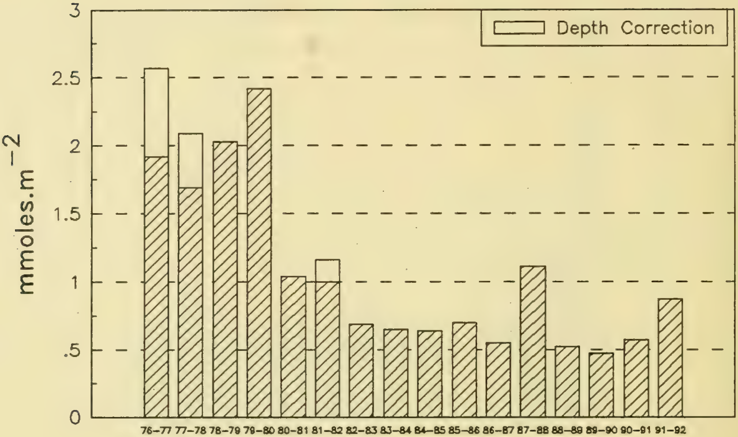
NITRATE

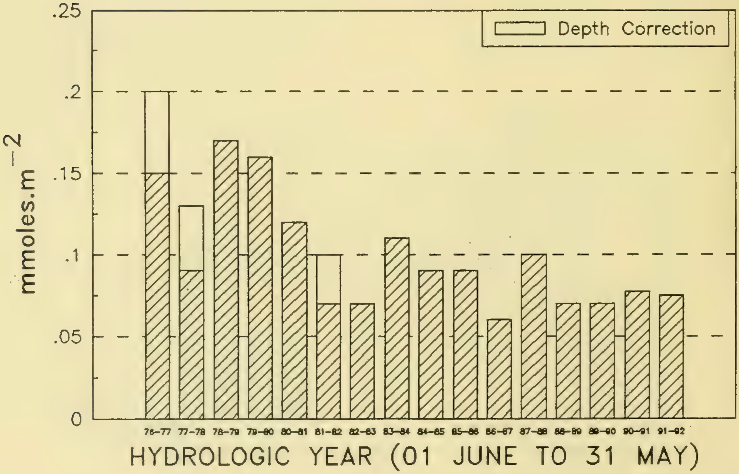
PHOSPHORUS



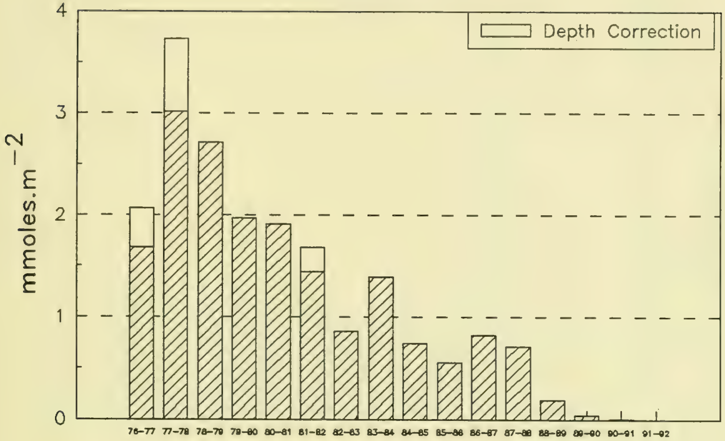
TOTAL KJELDAHL NITROGEN



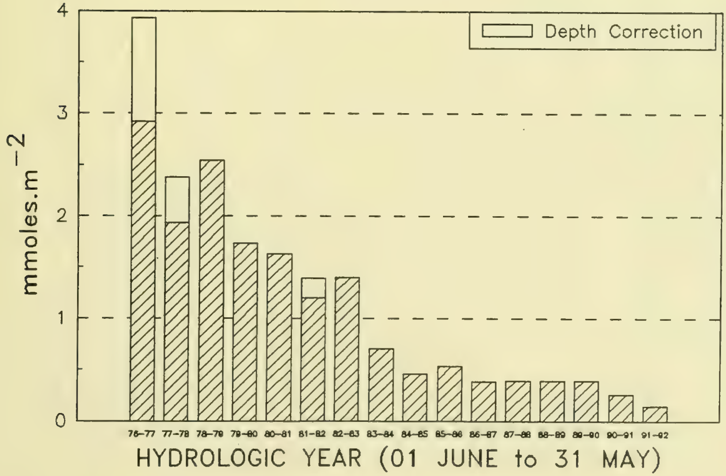

IRON


MANGANESE

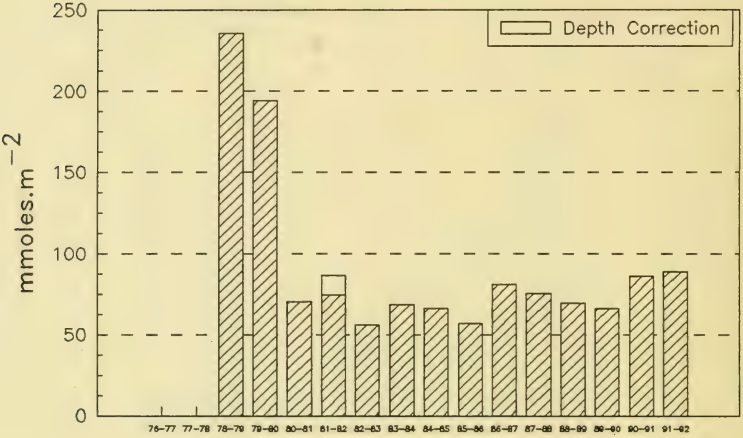
SILICATE



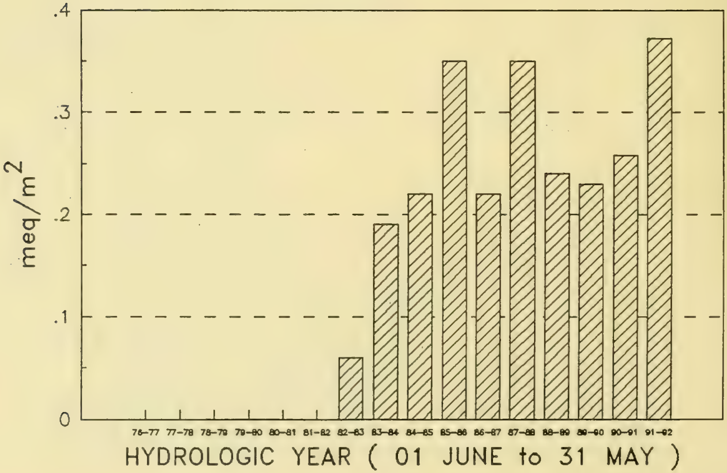
ALUMINUM



DISSOLVED ORGANIC CARBON



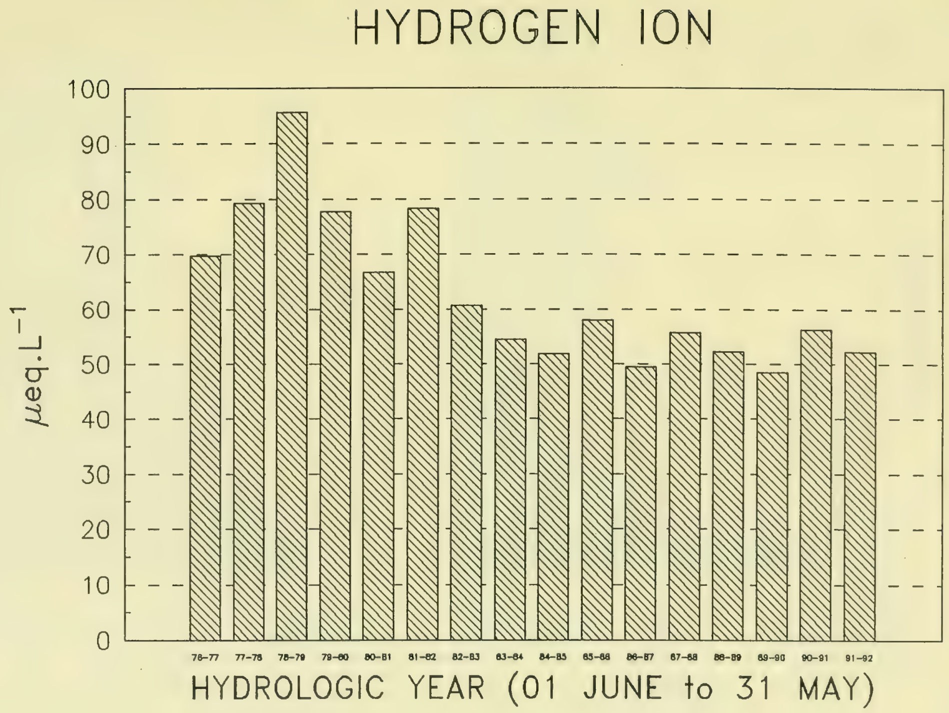
FLUORIDE

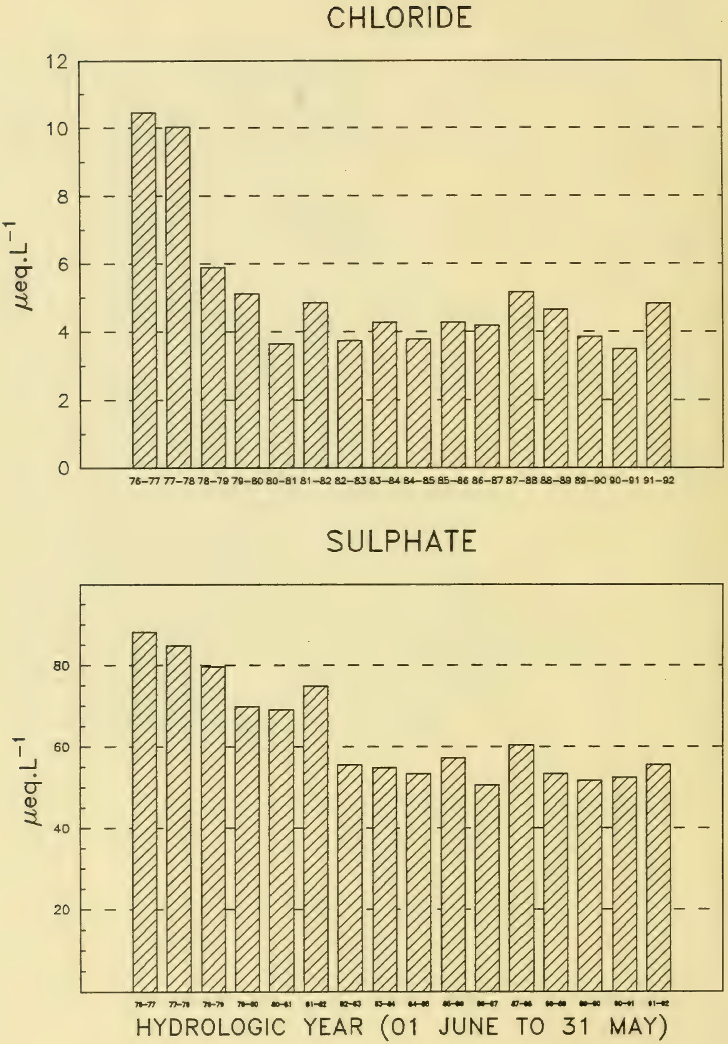


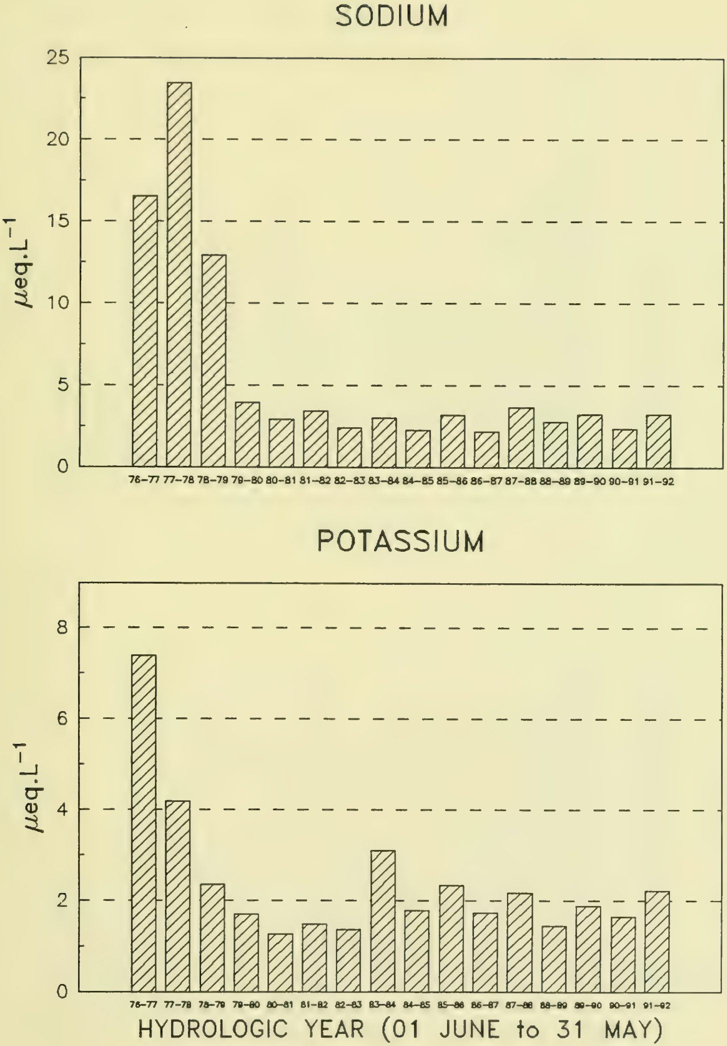
APPENDIX B

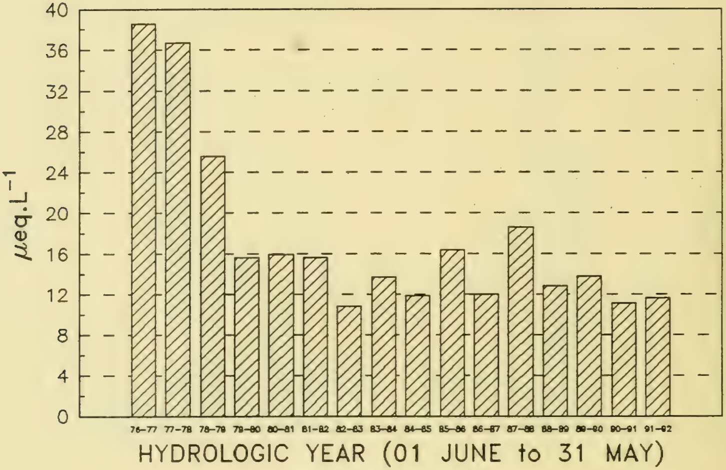
Annual Precipitation Centration

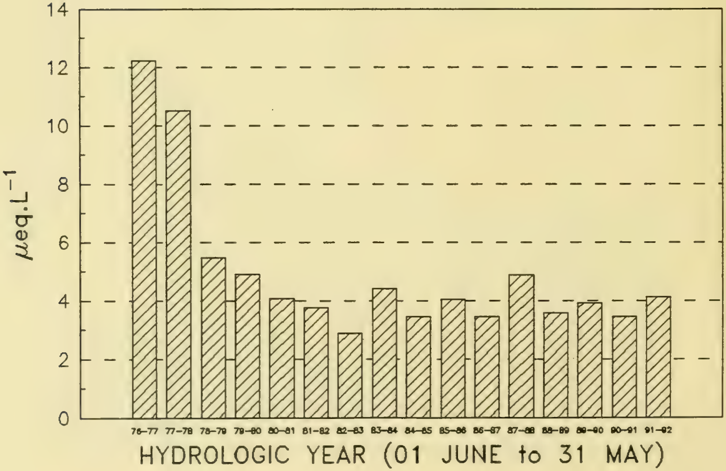
B1 Hydrogen Ion
B2 Chloride and Sulphate
B3 Sodium and Potassium
B4 Calcium and Magnesium
B5 Ammonium and Nitrate
B6 Phosphorus and TKN
B7 Iron and Manganese
B8 Silicate and Aluminum
B9 Dissolved Organic Carbon and Fluoride

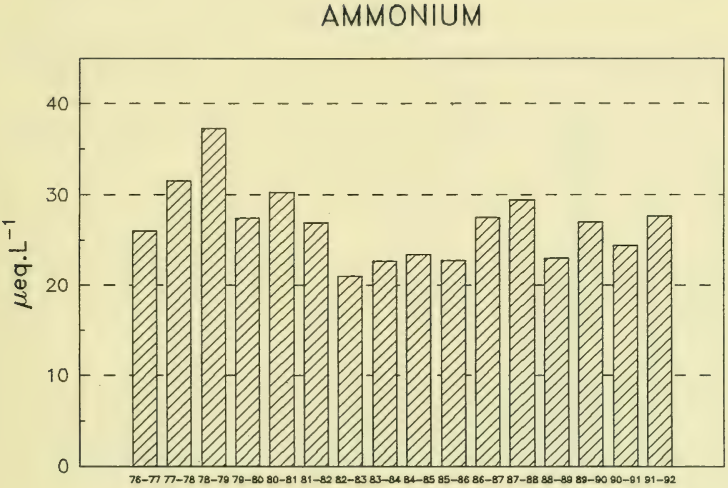

HYDROGEN ION
μeq.L⁻¹
100
90
80
70
60
50
40
30
20
10
0
76-77
77-78
78-79
79-80
80-81
81-82
82-83
83-84
84-85
85-86
86-87
87-88
88-89
89-90
90-91
91-92
HYDROLOGIC YEAR (01 JUNE to 31 MAY)

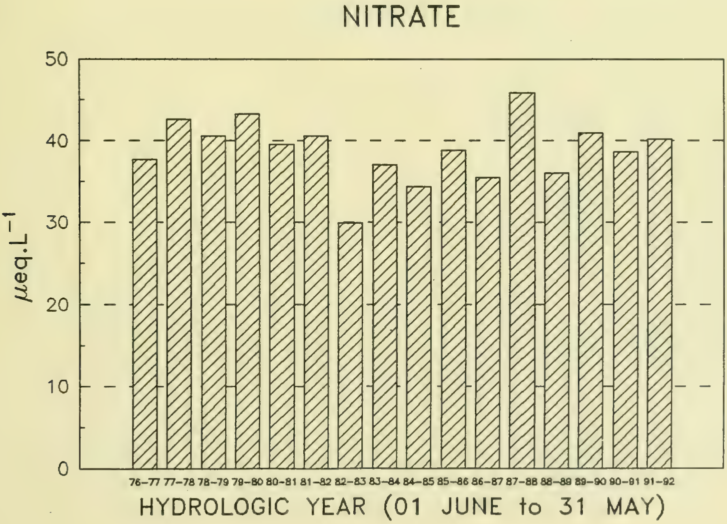

CHLORIDE
12
10
8
6
4
2
0
μeq.L^{-1}
76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85 85–86 86–87 87–88 88–89 89–90 90–91 91–92
SULPHATE
80
60
40
20
μeq.L^{-1}
76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85 85–86 86–87 87–88 88–89 89–90 90–91 91–92
HYDROLOGIC YEAR (01 JUNE TO 31 MAY)

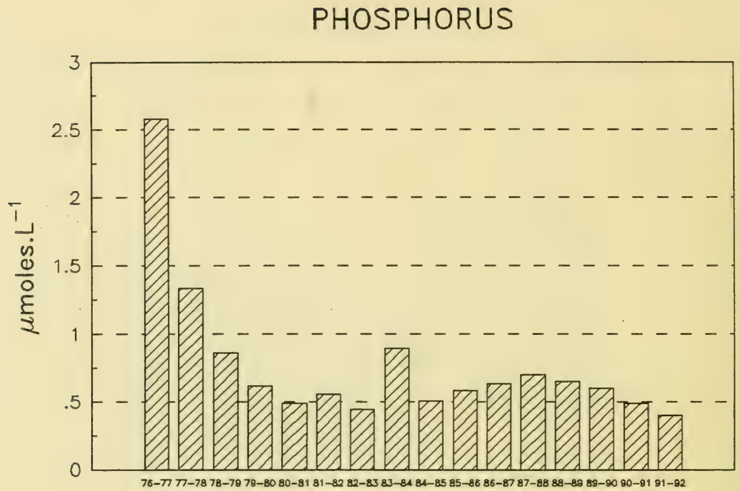
SODIUM
25
20
15
10
5
0
μeq.L^{-1}
76–77
77–78
78–79
79–80
80–81
81–82
82–83
83–84
84–85
85–86
86–87
87–88
88–89
89–90
90–91
91–92
POTASSIUM
8
6
4
2
0
μeq.L^{-1}
76–77
77–78
78–79
79–80
80–81
81–82
82–83
83–84
84–85
85–86
86–87
87–88
88–89
89–90
90–91
91–92
HYDROLOGIC YEAR (01 JUNE to 31 MAY)

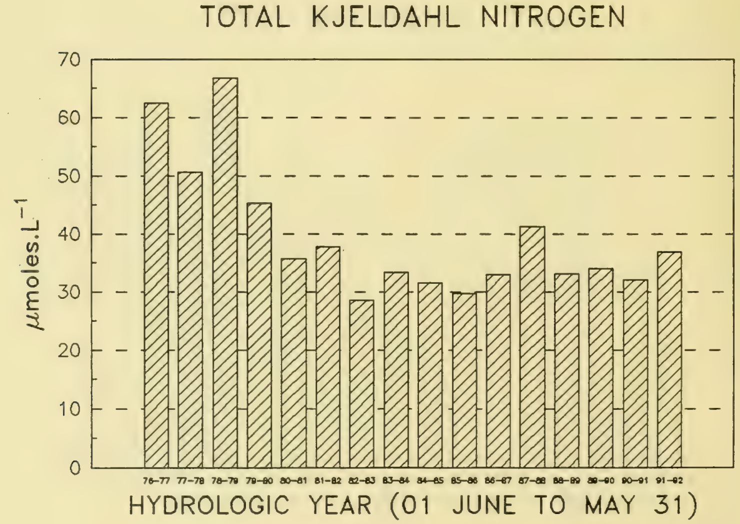

CALCIUM

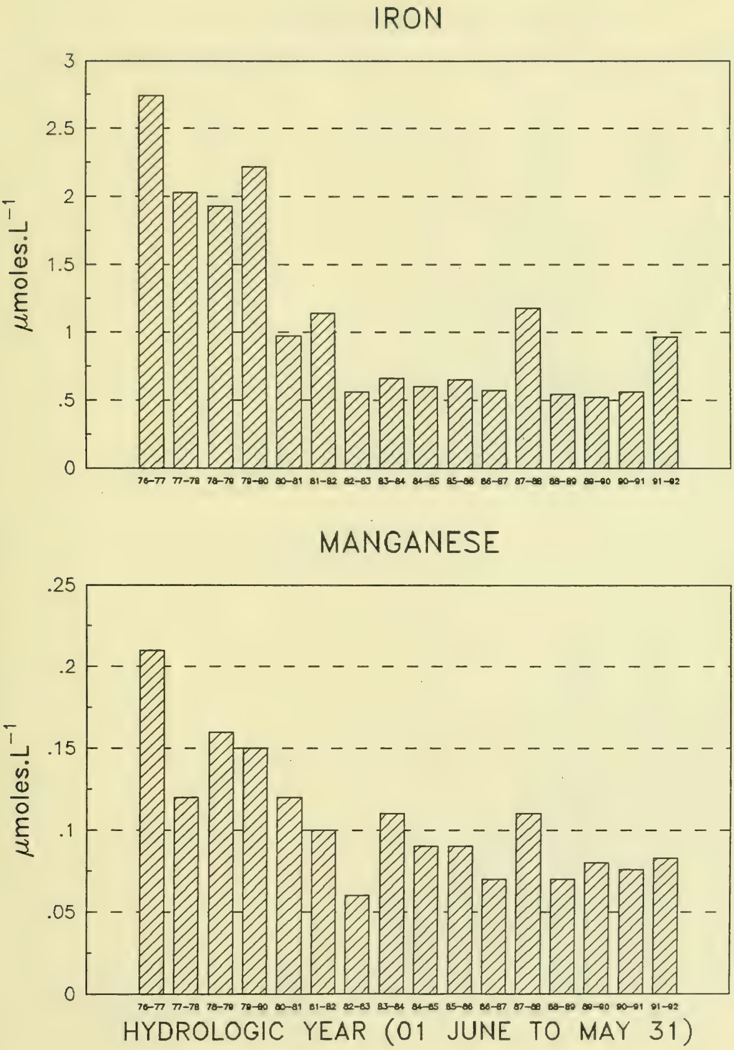

MAGNESIUM


AMMONIUM
μeq.L⁻¹
0
10
20
30
40
76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85 85–86 86–87 87–88 88–89 89–90 90–91 91–92


NITRATE
μeq.L⁻¹
0
10
20
30
40
50
76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85 85–86 86–87 87–88 88–89 89–90 90–91 91–92
HYDROLOGIC YEAR (01 JUNE to 31 MAY)


PHOSPHORUS
µmoles.L⁻¹
3
2.5
2
1.5
1
.5
0
76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85 85–86 86–87 87–88 88–89 89–90 90–91 91–92


TOTAL KJELDAHL NITROGEN
µmoles.L⁻¹
70
60
50
40
30
20
10
0
76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85 85–86 86–87 87–88 88–89 89–90 90–91 91–92
HYDROLOGIC YEAR (01 JUNE TO MAY 31)


IRON
μmoles.L^{-1}
0
.5
1
1.5
2
2.5
3
76-77
77-78
78-79
79-80
80-81
81-82
82-83
83-84
84-85
85-86
86-87
87-88
88-89
89-90
90-91
91-92
MANGANESE
μmoles.L^{-1}
0
.05
.1
.15
.2
.25
76-77
77-78
78-79
79-80
80-81
81-82
82-83
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84-85
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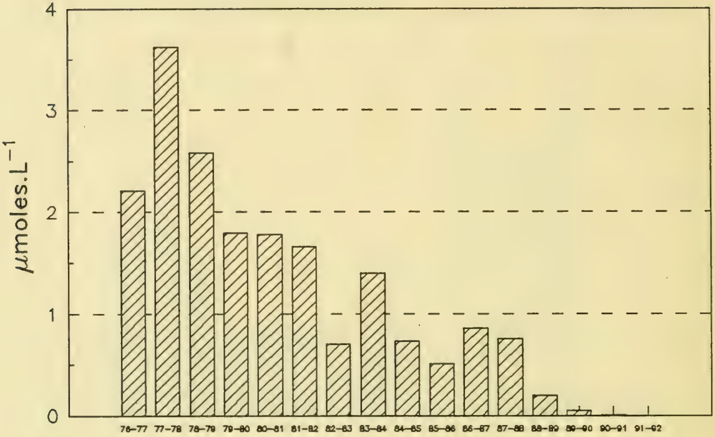
86-87
87-88
88-89
89-90
90-91
91-92
HYDROLOGIC YEAR (01 JUNE TO MAY 31)



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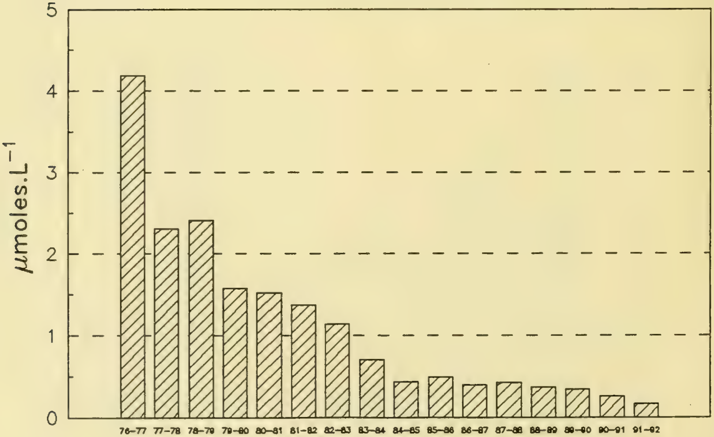
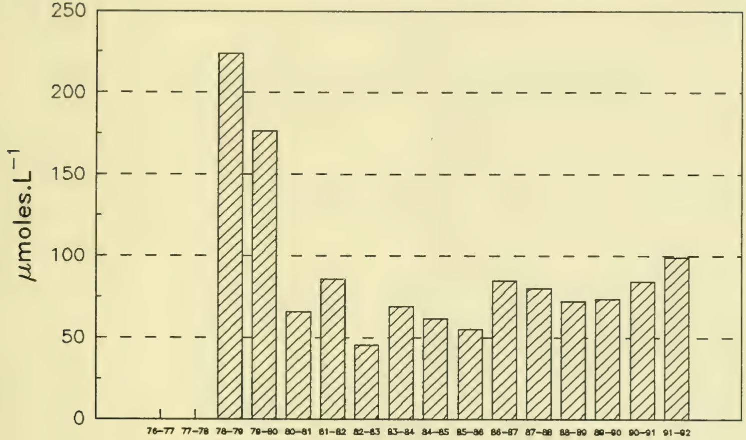
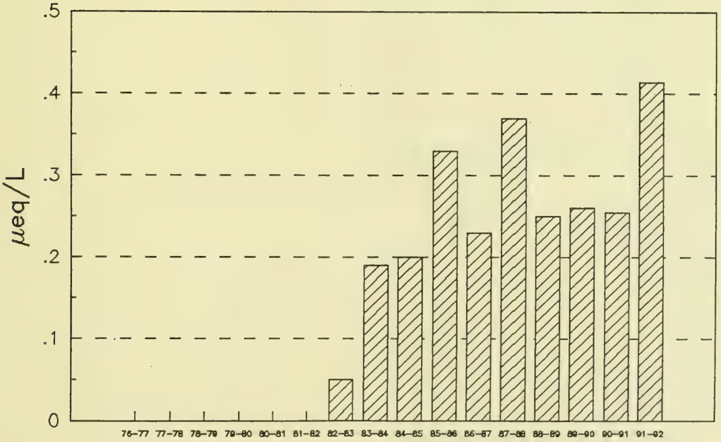


ALUMINUM



DISSOLVED ORGANIC CARBON



FLUORIDE

APPENDIX C

Analytical Methodology: History for Each Chemical Parameter

C1	Aluminum
C2	Ammonia
C3	Calcium
C4	Chloride
C5	Dissolved Organic Carbon
C6	Fluoride
C7	Hydrogen Ion (pH)
C8	Iron
C9	Magnesium
C10	Manganese
C11	Nitrogen-Nitrate
C12	Potassium
C13	Phosphorus
C14	Silicates
C15	Sodium
C16	Sulphate
C17	Nitrogen-Total Kjeldahl Nitrogen

Table C1 **Aluminum**

Identification: ALUT (total aluminum) in $\mu g/L$ or mg/L as Al

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1.	Laboratory:	Inorganic Trace Contaminants (ITC), Toronto, September 1976 - May 1978	
	Sampling:	Container -	500 mL or 1 L nitric acid washed nalgene (by Central Stores in Toronto)
		Field Collection -	76 μ filter, triple rinse with sample, preserved with 1 mL HNO_3, non-refrigerated until analysis
	Analysis:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)	
2.	Laboratory:	ITC, Toronto, May 1978 - May 1979	
	Sampling:	Container -	500 mL or 1 L nitric acid washed nalgene (by Central Stores in Toronto), storage prior to use filled with distilled water and fixed with 1 mL HNO_3
		Field Collection -	76 μ filter, triple rinse with sample, preserved with 1 mL HNO_3, non-refrigerated until analysis
	Analysis:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)	
3.	Laboratory:	ITC, Toronto, May 1979 - June 1, 1982	
	Sampling:	Container -	500 mL nitric acid washed nalgene (by Central Stores in Toronto, no other pre-rinse)
		Field Collection -	76 μ filter, triple rinse with sample, preserved with 1 mL HNO_3, non-refrigerated until analysis
	Analysis:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)	
4.	Laboratory:	ITC, Toronto, June 1, 1982 - August 10, 1982	
	Sampling:	Container -	250 mL polystyrene, plastic cap with no liner, rinsed with 5% Hcl and stored with 5% Hcl until use
		Field Collection -	76 μ filter, triple rinse with sample, preserved with 1 mL HNO_3, non-refrigerated until analysis, preservation with .5 mL HNO_3 (Aristar)
	Analysis	Automated modular continuous flow atomic absorption spectrophotometry (AAS)	
5.	Laboratory:	ITC, Toronto, August 10, 1982 - April 11, 1983	
	Sampling:	Container -	250 mL or 450 mL polystyrene, plastic cap with no liner, new recycled each sample, no special rinse
		Field Collection -	76 μ filter, triple rinse with sample, preserved with 1 mL HNO_3, non-refrigerated until analysis, preservation with .5 mL HNO_3 (Aristar)

Table C1 (cont'd.)

	Analysis:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)	
6.	Laboratory:	Dorset Lab, Dorset, April 11, 1983 - April 17, 1992	
	Sampling:	Container -	15 mL polypropylene or polystyrene culture tube with cap
		Field Collection -	86 μ filter, triple rinse with sample, polyester (Pecap) - refrigerated until analysis, preservation with .5 mL HNO_3 (Aristar), aliquot poured from 450 mL PET into 15 mL culture tube by lab after August 29, 1984
	Analysis:	Acidification to approximately 0.2% with ultraclean Aristar acid and refrigeration until analysis by graphite furnace atomic absorption	
7.	Laboratory:	Dorset Lab, April 21, 1992 until present	
	Sampling:	Container -	90 mL polystyrene bottle
		Field Collection -	The 90 mL sample is acidified by lab personnel to 0.1% with HNO_3 ultraclean (Aristar) acid and refrigerated until analysis. A 15 mL aliquot is poured into a culture tube just prior to analysis.
	Analysis:	A PCV/UV colourimetric technique (AAS).	

Table C2 **Ammonia**

Identification: NNHTFR (ammonium plus ammonia) in μ/L as N

1.	Laboratory:	Rivers and Lakes Lab, Toronto, June 1975 - April 1, 1977	
	Sampling:	Container -	1 L Boston glass
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	Ammonia plus ammonium ions are determined on the filtrate via the formation of indophenol blue in a buffered system using nitroprusside as a catalyst. A reference stream, which differs from the colour formation stream by replacement of the catalyst with an equal flow of water, is employed to suppress sample matrix effects. Approximate absorbance: 0.40 at the 1,000 μg/L as N level. N.B. Nitrate plus nitrite is determined simultaneously.	
	Instrumentation:	Basic automated modular continuous flow system plus the following modules: 2 of 37°C heating bath (7.7 mL delay). Colourimetric measurement is through a 5.0 cm light path at 630 nm. Two analytical ranges are obtained from the output of the colourimeter.	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 1 Detection criterion (T): 5	
2.	Laboratory:	Dorset Lab, Dorset, April 1977 - August 1979	
	Sampling:	Container -	125 mL Prince of Wales, acid base bath, then distilled water rinse
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation, but with filtration through Gelman .45 μ membrane filter
	Analysis:	Modified automated phenate-hydrochloride method with sodium nitroprusside	
3.	Laboratory:	Dorset Lab, Dorset, August 1979 - June 1, 1982	
	Sampling:	Container -	500 mL or 1 L nalgene, acid base bath, then distilled water rinse
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation, .45 μ filtration by chemistry lab
	Analysis:	Modified automated phenate-hydrochloride method with sodium nitroprusside	
4.	Laboratory:	Dorset Lab, Dorset, June 1, 1982 - present	
	Sampling:	Container -	450 mL polystyrene and PET bottle with non-pulp lined cap
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation, .45 μ filtration by chemistry lab
	Analysis	Modified automated phenate-hydrochloride method with sodium nitroprusside	

Table C3 **Calcium**

Identification: CAUR in mg/L as Ca

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1. Laboratory: Rivers and Lakes Lab, Toronto, April 1, 1974 - May 17, 1979

Sampling:
Container - 1 L Boston glass
Field Collection - 76 μ filter, triple rinse, no preservation, refrigerate

Analysis: Samples are analyzed by AAS at 422.7 nm using an air/acetylene flame. Acidified lanthanum chloride is added as a releasing agent via an automated sampling train. Approximate absorbance: RMCAMGH: 0.9, RMCAMGL: 0.5; full scale values

Instrumentation: Automated modular continuous flow atomic absorption spectrophotometry (AAS)

Reporting:
Maximum significant figures: 3
Minimum increment (W): 0.2, 0.01
Detection limit (T): 0.3, 0.02

2. Laboratory: Precipitation Lab, Toronto, May 18 1979 - present

Sampling:
Container - 450 mL polystyrene
Field Collection - 76 μ filter, triple rinse, no preservation, refrigerate

Analysis: Samples are analyzed by AAS at 422.7 nm with an air/acetylene flame. Acidified lanthanum chloride is added as a releasing agent via an automated sampling train. Approximate absorbance: 0.2 at the 2.00 mg/L level

Instrumentation: Automated modular continuous flow atomic absorption spectrophotometry (AAS)

Reporting:
Maximum significant figures: 3
Minimum increment (W): 0.01
Detection limit (T): 0.04

Table C4 **Chloride**

Identification: CLIDUR in mg/L as Cl

1.	Laboratory:	Rivers and Lakes Lab, Toronto, May 1, 1975 - March 30, 1978
	Sampling:	Container - 1 L Boston glass Field Collection - 76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	Chloride ions are combined with mercuric thiocyanate releasing thiocyanate quantitatively. Thiocyanate then reacts with ferric ions to produce ferric thiocyanate (red), and the absorbance of the latter is measured colourimetrically. A reference stream, from which mercuric thiocyanate has been eliminated is utilized to compensate for sample matrix effects. Approximate absorbance: 0.3 at the 50 mg/L level. N.B. Reactive silicates are determined simultaneously.
	Instrumentation:	Boxed FIA system consisting of basic automated modular continuous flow system plus the following modules: sample injection valves with air flow controls, timer, bubble gate. Colourimetric measurement is through a 1.5 cm light path at 470 nm. Two analytical ranges are obtained from the output of the colourimeter.
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.05 Detection limit (T): 0.09
2.	Laboratory:	Precipitation Lab, Toronto, April 1, 1978 - present
	Sampling:	Container - April 1, 1978 - May 30, 1982: 1 L Boston glass June 1, 1982 - present: 450 mL polystyrene Field Collection - 76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	Chloride is separated from other anions in the sample by automated suppressed ion chromatography using an eluent mixture of 0.003M sodium bicarbonate and 0.0024M sodium carbonate with conductivity detection. Samples are spiked with $Na_2CO_3/NaHCO_3$ to match the eluent strength and maintain background conductivity. The concentration of chloride in mg/L as Cl is determined by comparison of the sample scan to a series of standard scans. Full scale conductivity: 10 μS/cm. Nitrate and sulphate are determined simultaneously.
	Instrumentation:	Basic modular continuous flow ion chromatographic system plus microcomputer for automated sample introduction and timing
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.01 Detection limit (T): 0.03

Table C5 **Dissolved Organic Carbon**

Identification: DOC in mg/L as C

1.	Laboratory:	Rivers and Lakes Lab, Toronto, June 1975 - April 4, 1978
	Sampling:	Container - June 1975 - April 1978: 1 L Boston glass Field Collection - 76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	Both total carbon and inorganic carbon are determined by direct analysis on a liquid sample. The organic carbon component is obtained by taking the difference between the total carbon and the inorganic carbon. The total organic carbon generally relates directly to the BOD and COD, but this relationship depends upon the nature of the organic material in the sample. Total carbon is determined by injecting a known volume of sample onto a hot catalyst using a hypodermic syringe. The CO_2 gas produced on combustion is measured by infra-red spectrophotometry. Inorganic carbon is determined by acidifying a known volume of sample in a closed chamber and the released CO_2 gas measured by infra-red spectrophotometry. Results are reported in mg/L of carbon.
2.	Sampling:	Container - April 4, 1978 - June 1, 1982: 1 L Boston glass Field Collection - 76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	Using an automated system, the supernatant from a settled sample is acidified and flushed with nitrogen gas (500 mL/min) to remove inorganic carbon. Organic carbon is then oxidized to carbon dioxide gas by exposure to ultra-violet light (UV) in acid persulphate media. The gas then passes through a gas permeable membrane into a weakly buffered alkaline phenolphthalein solution. The decrease in absorbance of this coloured solution is a measure of the dissolved organic carbon content of the sample. Approximate absorbance: 0.3 at the 20 mg/L level. N.B. Dissolved inorganic carbon is determined simultaneously.
	Instrumentation:	Basic automated modular continuous flow system plus the following modules: nitrogen and air (CO_2 free) gas supplies with flow controls, dialysis unit, UV digester. Colourimetric measurement is through a 5.0 cm light path at 550 nm.
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.1 Detection limit (T): 0.2
3.	Sampling:	Container - June 1, 1982 - present: 450 mL polystyrene with non-pulp lined plastic cap Field Collection - 76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis	Using an automated system, the supernatant from a settled sample is acidified and flushed with nitrogen gas (500 mL/min) to remove inorganic carbon. Organic carbon is then oxidized to carbon dioxide gas by exposure to ultra-violet light (UV) in acid persulphate media. The gas then passes through a gas permeable membrane into a weakly buffered alkaline phenolphthalein solution. The decrease in absorbance of this coloured solution is a measure of the dissolved organic carbon content of the sample. Approximate absorbance: 0.3 at the 20 mg/L level. N.B. Dissolved inorganic carbon is determined simultaneously.

Table C6		**Fluoride**	
Identification:		FFIDUR in μg/L as F	
	Sample Type:	Streams, lakes, precipitation	
1.	Laboratory:	Domestic Water, Toronto, April 11, 1983 - April 1, 1986	
	Sampling:	Container -	450 mL polystyrene with non-pulp lined cap
		Field Collection -	76 μ filter, triple rinse, no refrigeration until analysis
	Analysis:	Alizarin Blue colourimetry, free fluoride selective electrode (Orion)	
2.	Laboratory:	Dorset Soils Lab, Dorset, April 1, 1986 - present	
	Sampling:	Container -	450 mL polystyrene with non-pulp lined cap
		Field Collection -	76 μ filter, triple rinse, no refrigeration until analysis
	Analysis:	Fluoride ion specific electrode, total ionic strength adjustment buffer containing phosphoric acid, sodium nitrate, di-sodium EDTA, sodium chloride and sodium hydroxide to a pH of 6.7. Automated system using Technicon Ion specific electrode module (range = 0 to 70 μg/L).	

Table C7 **Hydrogen Ion**

Identification: pH

1.	Laboratory:	River Lab, Toronto, June 1975 - September 1976	
	Sampling:	Container -	1 L Boston glass, new recycled every time
		Field Collection -	76 μ filter, triple rinse
	Analysis:	Measurement at room temperature, Corning meter with Corning or Fischer electrodes	
2.	Laboratory:	Vankoughnet Lab, June 1976 - September 1976 Dorset Lab, October 1976 - June 1978	
	Sampling:	Container -	1 L nalgene, H_2SO_4 and NaOH bath with distilled water rinse
		Field Collection -	76 μ filter, triple rinse
	Analysis:	Measurement at room temperature, Corning meter with Corning or Fischer electrodes	
3.	Laboratory:	Dorset Lab, Dorset, June 1978 - June 1, 1982	
	Sampling:	Container -	1 L nalgene, H_2SO_4 and NaOH bath with distilled water rinse
		Field Collection -	76 μ filter, triple rinse
	Analysis:	Radiometer pH meter, Corning or Fischer electrodes, analysis at room temperature	
4.	Laboratory:	Dorset Lab, Dorset, June 1, 1982 - present	
	Sampling:	Container -	250 mL opaque brown nalgene
		Field Collection -	76 μ filter, triple rinse
	Analysis	pH is directly measured on a stirred sample (100 mL) at room temperature. Stirring rate, tube size, degree of electrode immersion and room temperature range are uniform for all samples and standards. N.B. Alkalinity (Gran) or Acidity (Total Fixed Endpoint) is determined simultaneously.	
	Instrumentation:	Semi-automated modular titration system with microcomputer control and data reduction software	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.01	

Table C8 **Iron**

Identification: FEUT in mg/L as Fe

1.	Laboratory:	Rivers and Lakes Lab, Toronto, April 20, 1976 - October 1979 Precipitation Lab, Toronto, October 1979 - July 1, 1985	
	Sampling:	Container - Field Collection -	April 1976 - June 1, 1982, 1 L Boston glass 76 μ filter, triple rinse, refrigeration until analysis
	Analysis:	Samples (20.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous-2, 4, 6-tri (2'pyridyl) - l, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Manganese is determined simultaneously. Test Method: 535AF1 (Precip FAAS) *	
	Instrumentation:	Culture tubes with silicone rubber septa and tube racks constructed to maintain seal during digestion step. Autoclave plus basic automated modular continuous flow system with colourimetric measurement through a 5.0 cm light path at 600 nm.	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.01 Detection limit (T): 0.03	
2.	Sampling:	Container - Field Collection -	June 1, 1982 - August 10, 1982: 250 mL polystyrene, rinsed with 5% HCl and stored with HCl, samples taken at this time preserved with 0.5 mL Aristar HNO_3 76 μ filter, triple rinse, refrigeration until analysis
	Analysis:	Samples (20.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous-2, 4, 6-tri (2'pyridyl) - l, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Test Method: 522AA5 (HNO_3 Prec mics AAS BKGD) *	
3.	Sampling:	Container - Field Collection -	August 10, 1982 - July 1, 1985: 450 mL polystyrene, no pre-rinsing or preservative 76 μ filter, triple rinse, refrigeration until analysis
	Analysis:	Samples (20.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous-2, 4, 6-tri (2'pyridyl) - l, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Test Method: 535AF1 (Precip FAAS) *	
4.	Laboratory:	(Inorganic Trace Contaminants) ITC, Toronto, July 1, 1985 - June 24, 1991	
	Sampling:	Container -	July 1, 1985 - November 8, 1985: 450 mL polystyrene, no pre-rinsing, no preservative November 8, 1985 - June 26, 1986, 100 mL polystyrene vial, no preservative June 26, 1986 - June 24, 1991, 100 mL polystyrene vial, acidified by Dorset chem lab prior to shipment to ITC for analysis

Table C8 (cont'd.)

		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis	July 1, 1985 - August 1, 1985 - as above Test Method: 536BA1 (Precon AAS) August 1, 1985 - June 16, 1986, ICP (Iriductive Coupled Plasma) mass spectrophotometry using plasma as source for spectrophotometer. Test Method: 001AE5 (run straight ICP MS), 522AE2 (HNO_3 Prec ICP)*	
5.	Laboratory:	Dorset Soils Lab, Dorset, June 24, 1991 - present	
	Sampling:	Container -	100 mL polystyrene vial, acidified at lab with 0.25 mL conc HNO_3
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis:	Samples (40.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous-2, 4, 6-tri (2'pyridyl) - 1, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Test Method: 504BC2 (Autoclave/Auto TPTZ)	
	Instrumentation:	Culture tubes with teflon lined caps and tube racks constructed to maintain seal during digestion step. Autoclave plus basic automated modular continuous flow system with colourimetric measurement through a 5.0 cm light path at 600 nm.	
	Reporting:	Minimum increment (W): 1 μg/L Detection Limit (T): 5 μg/L	

* Note: Test Method codes may not be entirely reliable sources of analytical methods. Different labs may use the same or different instruments with the same method and thus, use different method codes. Some method codes may refer to the same method and same lab, but differ due to method code reorganization schemes (ITC especially).

Table C9 **Magnesium**

Identification: MGUR in mg/L as Mg

1.	Laboratory:	Rivers and Lakes Lab, Toronto, April 1, 1974 - May 17, 1979
	Sampling:	Container - 1 L Boston glass Field Collection - 76 μ filter, triple rinse, refrigeration
	Analysis:	Samples are analyzed by AAS at 285.2 nm using an air/acetylene flame. Acidified lanthanum chloride is added as a releasing agent via an automated sampling train. Approximate absorbance: 0.9 at full scale for both analytical ranges
	Instrumentation:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.02, 0.01 Detection limit (T): 0.09, 0.02
2.	Laboratory:	Precipitation Lab, Toronto, May 18, 1979 - present
	Sampling:	Container - 450 mL polystyrene Field Collection - 76 μ filter, triple rinse, refrigeration
	Analysis:	Samples are analyzed by AAS at 285.2 nm with an air/acetylene flame. Acidified lanthanum chloride is added as a releasing agent via an automated sampling train. Approximate absorbance: 0.5 at the 0.50 mg/L level.
	Instrumentation:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.005 Detection limit (T): 0.008

Table C10 **Manganese**

Identification: MNUT in mg/L as Mn

1.	Laboratory:		Rivers and Lakes Lab, Toronto, April 20, 1976 - October 1979 Precipitation Lab, Toronto - October 1979 - July 1, 1985
	Sampling:	Container -	April 1976 - June 1, 1982: 1L Boston glass
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis:		Samples (20.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous 2, 4, 6-tri (2' pyridly) - 1, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Iron is determined simultaneously. Test Method: 535AF1 (Precip FAAS) *
	Instrumentation:		Culture tubes with silicone rubber septa and tube racks constructed to maintain seal during digestion step. Autoclave plus basic automated modular continuous flow system with colourimetric measurement through a 5.0 cm light path at 600 nm.
	Reporting:		Maximum significant figures: 3 Minimum increment (W): 0.001 Detection limit (T): 0.03
2.	Sampling:	Container -	June 1, 1982 - August 10, 1982: 250 mL polystyrene, rinsed with 5% Hcl and stored with Hcl, samples taken at this time preserved with 0.5 mL Aristar HNO_3
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis:		Samples (20.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous 2, 4, 6-tri (2' pyridly) - 1, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Iron is determined simultaneously. Test Method: 522AA5 (HNO_3 Prec misc AAS BKGD) *
3.	Sampling:	Container -	August 10, 1982 - July 1, 1985: 450 mL polystyrene, no pre-rinsing or preservative
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis:		Samples (20.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous 2, 4, 6-tri (2' pyridly) - 1, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Iron is determined simultaneously. Test Method: 535AF1 (Precip FAAS) *
4.	Laboratory:		Inorganic Trace Contaminants (ITC), Toronto, July 1, 1985 - June 24, 1991
	Sampling:	Container -	July 1, 1985 - November 8, 1985: 450 mL polystyrene, no pre-rinsing or preservative November 8, 1985 - June 26, 1986: 100 mL polystyrene vial, no preservative June 26, 1986 - June 24, 1992: 100 mL polystyrene vial, acidified by Dorset chem lab prior to shipment to ITC for analysis.

Table C10 (cont'd.)

		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis:		July 1, 1985 - August 1, 1985 - Samples (20.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous 2, 4, 6-tri (2' pyridly) - 1, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Iron is determined simultaneously. Test Method: 536BA1 (Precon AAS) August 1, 1985 - June 26, 1986 - ICP (Iriductive Coupled Plasma) mass spectrophotometry using plasma as source for spectrophotometer. Test Method: 001AE5 (run straight ICP MS), 522AE2 (HNO_3 Prec ICP) *
5.	Laboratory:		Dorset Soils Lab, Dorset, June 24, 1991 - present
	Sampling:	Container -	100 mL polystyrene vial, acidified at lab with 0.25 mL conc HNO_3
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis:		Samples (40.0 mL) are autoclaved in sulphuric acid hydroxylamine media at 121°C for 30 min. The iron content of the digestate is determined colourimetrically by formation of the ferrous 2, 4, 6-tri (2' pyridly) - 1, 3, 5-triazine (TPTZ) complex in a buffered system. Approximate absorbance: 0.3 at the 1.0 mg/L level. Test Method: 504BC2 (Autoclave/Auto TPTZ)
	Instrumentation:		Culture tubes with teflon lined caps and tube racks constructed to maintain seal during digestion step. Autoclave plus basic automated modular continuous flow system with colourimetric measurement through a 5.0 cm light path at 600 nm.
	Reporting:		Minimum increment (W): 1 μg/L Detection Limit (T): 5 μg/L

* Note: Test Method codes may not be entirely reliable sources of analytical methods. Different labs may use the same or different instruments with the same method and thus, use different method codes. Some method codes may refer to the same method and same lab, but differ due to method code reorganization schemes (ITC especially).

Table C11 **Nitrogen**

Identification: NNOTFR (nitrate plus nitrite) in μg/L as N

1.	Laboratory:	Rivers and Lakes Lab, Toronto, June 1975 - April 1, 1977	
	Sampling:	Container -	1 L Boston glass
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	Nitrate plus nitrite is determined on the filtrate of a sample. Nitrate is reduced to nitrite in alkaline media at 37°C by hydrazine sulphate with copper as a catalyst. Colourimetry is based on the formation of an azo dye by nitrite, sulphanilamide, and N (1-napthyl) ethylenediaminedihydrochloride. To control metal ion interference, samples are passed through an ion exchange column prior to the reduction step. Approximate absorbance: 0.5 at the 500 μg/L as N level. N.B. Ammonia plus ammomium is determined simultaneously.	
	Instrumentation:	Basic automated modular continuous flow system plus the following modules: 37°C heating bath (7.7 mL delay), ion exchange column. Colourimetric measurement is through a 5.0 cm light path at 520 nm.	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 2 Detection criterion (T): 3	
2.	Laboratory:	Dorset lab, Dorset, April 1977 - August 1979	
	Sampling:	Container -	125 mL Prince of Wales, acid base bath, then distilled water rinse
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation, but with filtration through .45 μ membrane filters
	Analysis:	Hydrazine reduction method, automated deazotization colourimetry	
3.	Laboratory:	Dorset Lab, Dorset, August 1979 - June 1, 1982	
	Sampling:	Container -	500 mL or 1 L nalgene, acid base bath, then distilled water rinse
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation, but filtration by chemistry lab
	Analysis:	Hydrazine reduction method, automated deazotization colourimetry	
4.	Laboratory:	Dorset Lab, Dorset, June 1, 1982 - present	
	Sampling:	Container -	450 mL polystyrene and PET bottle with non-pulp lined cap
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation, but filtration by chemistry lab
	Analysis	Hydrazine reduction method, automated deazotization colourimetry	

Table C12 **Potassium**

Identification: KKUR in mg/L as K

1.	Laboratory:	Rivers and Lakes Lab, Toronto, April 1, 1974 - May 17, 1979	
	Sampling:	Container - Field Collection -	1 L Boston glass 76 μ filter, triple rinse, refrigeration
	Analysis:	Samples are analyzed by AAS at 766.5 nm using an air/acetylene flame. Cesium is added as a suppressant via an automated sampling train. Approximate absorbance: RMNAKH: 0.9, RMNAKL: 0.54; full scale values	
	Instrumentation:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.02, 0.01 Detection limit (T): 0.04, 0.03	
2.	Laboratory:	Precipitation Lab, Toronto, May 18, 1979 - present	
	Sampling:	Container - Field Collection -	450 mL polystyrene 76 μ filter, triple rinse, refrigeration
	Analysis:	Samples are analyzed by AAS at 766.5 nm with an air acetylene flame. Cesium is added as a suppressant via an automated sampling train. Approximate absorbance: 0.5 at the 1.00 mg/L level	
	Instrumentation:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.005 Detection limit (T): 0.014	

Table C13 **Phosphorus**

Identification: PPUT (total phosphorus) in μg/L as P

1.	Laboratory:	Rivers and Lakes Lab, Toronto, June 1975 - March 1976	
	Sampling:	Container -	1 L Boston glass
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis:	Automated Stannous chloride molybdate reduction, hotplate digestion with AAII system	
2.	Laboratory:	Vankoughnet and Dorset Labs, March 1976 - September 1976	
	Sampling:	Container -	125 erlenmeyer flasks, acid base distilled water bathed, then oven heated, covered with parafilm
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis
	Analysis:	Automated Stannous chloride molybdate reduction, hotplate digestion with AAII system	
3.	Laboratory:	Dorset Lab, Dorset,	
	Sampling:	Container -	September 1976 - September 1, 1979: 50 mL pyrex culture tubes with teflon lined caps, autoclaved by chemistry lab
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, filled directly with station sample water, or poured from nutrient sample in the lab; after December 1979 triplicate samples were taken, prior to that duplicate were collected
	Analysis:	Automated Stannous chloride molybdate reduction, hotplate digestion with AAII system. March 22, 1979 - December 1979: duplicate samples. December 1979 - March 20, 1981: triplicate samples. March 20, 1981 - present, duplicate samples.	
4.	Laboratory:	Dorset Lab, Dorset, September 1, 1979 - present	
	Sampling:	Container -	50 mL pyrex culture tubes with teflon lined caps, autoclaved by chemistry lab
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, filled directly with station sample water, or poured from nutrient sample in the lab; after December 1979 triplicate samples were taken, prior to that duplicate were collected
	Analysis:	After withdrawal of excess volume, digestion reagent is added and samples are autoclaved in sulphuric acid potassium persulphate media at 121°C for 60 min. The orthophosphate content of the digestate is determined colourimetrically by formation of the reduced phospho-antimonyl-molybdate complex using ascorbic acid as the reducing agent. Approximate absorbance: 0.3 at the 200 μg/L as P level.	
	Instrumentation:	Autoclave plus basic automated modular continuous flow system with colourimetric measurement through a 5.0 cm light path at 880 nm using appropriate phototube. Two analytical ranges are obtained from the output of the colourimeter.	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.1 Detection limit (T): 0.2	

Table C14 **Silicon Reactive Silicates**

Identification: SIO_3UR mg/L as Si

1.	Laboratory:	Rivers and Lakes Lab, Toronto, February 1, 1975 - present	
	Sampling:	Container -	1 L Boston glass, new, reground each sample
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	Reactive silicates are determined by formation of a reduced molybdo-silicate complex at pH 1.6, using ascorbic acid as the reducing agent, and oxalic acid to suppress phosphate interference. Approximate absorbance: 0.7 at the 5.0 mg/L as Si level. N.B. Chloride is determined simultaneously.	
	Instrumentation:	Boxed FIA system consisting of basic automated modular continuous flow systemm plus the following modules: sample injection valve with air flow controls, timer, bubble gate. Colourimetric measurement is through a 5.0 cm light path at 660 nm.	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.02 Detection limit (T): 0.06	
2.	Sampling:	Container -	January 1, 1982 - June 1, 1982: 250 mL polystyrene with non-pulp lined plastic cap
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	Reactive silicates are determined by formation of a reduced molybdo-silicate complex at pH 1.6, using ascorbic acid as the reducing agent, and oxalic acid to suppress phosphate interference. Approximate absorbance: 0.7 at the 5.0 mg/L as Si level. Chloride is determined simultaneously.	
3.	Sampling:	Container -	June 1, 1982 - present: 450 mL polystyrene, with non-pulp lined plastic cap
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	June 1, 1982 - June 1, 1983 - Reactive silicates are determined by formation of a reduced molybdo-silicate complex at pH 1.6, using ascorbic acid as the reducing agent, and oxalic acid to suppress phosphate interference. Approximate absorbance: 0.7 at the 5.0 mg/L as Si level. N.B. Chloride is determined simultaneously.	
4.	Sampling:	Container -	450 mL polystyrene, with non-pulp lined plastic cap
		Field Collection -	76 μ filter, triple rinse, refrigeration until analysis, no preservation
	Analysis:	June 1, 1983 - present - Fixed flow injection system introduced, no changes in analytical ranges	

Table C15 **Sodium**

Identification: NAUR in mg/L as Na

1.	Laboratory:	Rivers and Lakes Lab, Toronto, April 1, 1974 - May 17, 1979
	Sampling:	Container - 1 L Boston glass Field Collection - 76 μ filter, triple rinse, refrigeration
	Analysis:	Samples are analyzed by AAS at 589.0 nm using an air acetylene flame. Cesium is added as a suppresant via an automated sampling train. Approximate absorbance: 0.9 for both analytical ranges
	Instrumentation:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.05, 0.01 Detection limit (T): 0.1, 0.03
2.	Laboratory:	Precipitation Lab, Toronto, May 18, 1979 - present
	Sampling:	Container - 450 mL polystyrene Field Collection - 76 μ filter, triple rinse, refrigeration
	Analysis:	Samples are analfyzed by AAS at 589.0 nm with an air acetylene flame. Potassium is added as a suppresant via an automated sampling train. Approximate absorbance: 0.5 at the 1.00 mg/L level.
	Instrumentation:	Automated modular continuous flow atomic absorption spectrophotometry (AAS)
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.005 Detection limit (T): 0.02

Table C16 **Sulphate**

Identification: SSO$_4$UR in mg/L as SO$_4$

1.	Laboratory:	Rivers and Lakes Lab, Toronto, June 1, 1975 - March 1978	
	Sampling:	Container - Field Collection -	1 L Boston glass 76 μ filter, triple rinse, no preservation
	Analysis:	Sample is pumpted through an ion exchange column to suppress cationic interferences, and then the sulphate reacts with barium emthyl-thymol blue (MTB). The absorbance of MTB provides a measurement of the sulphate concentration. Approximate absorbance: 1.0 at the 100 mg/L level.	
	Instrumentation:	Basic automated modular continuous flow system plus the modules: 37°C heating bath (7.7 mL delay), cationic exchange column. Colourimetric measurement is through a 55.0 cm light path at 460 nm.	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.5 Detection limit (T): 1.6	
2.	Laboratory:	Precipitation Lab, Toronto, April 1, 1978 - present	
	Sampling:	Container - Field Collection -	June 1, 1982 - present: 450 mL polystyrene 76 μ filter, triple rinse, no preservation
	Analysis:	Sulphate is separated from other anions in the sample by automated suppressed ion chromatography using an eluent mixture of 0.003M sodium bicarbonate and 0.002M sodium carbonate with conductivity detection. Samples are spiked with Na2CO$_3$/NaHCO$_3$ to match the eluent strength and mainntain background conductivity. The concentration of sulphate in mg/L as SO$_4$ is determined by comparison of the sample scan to a series of standard scans. Full scale conductivity: 10 μS/cm.	
	Instrumentation:	Basic modular continuous flow ion chromatographic system plus microcomputer for automated sample introduction and timing.	
	Reporting:	Maximum significant figures: 3 Minimum increment (W): 0.05 Detection limit (T): 0.07	

Table C17 **Nitrogen**

Identification: NNTKUR (total Kjeldahl nitrogen) in μg/L as N

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1. Laboratory: Rivers and Lakes Lab, Toronto, June 1975 - September 1976

   Sampling:
   Container - 1 L Boston glass
   Field Collection - 76 μ filter, triple rinse, refrigeration

   Analysis: Persulphate digestion (hot plate)

2. Laboratory: Dorset Lab, Dorset, September 1976 - August 1979

   Sampling:
   Container - 125 mL Prince of Wales, acid base bath, then distilled water rinse
   Field Collection - 76 μ filter, triple rinse, refrigeration

   Analysis:
   September 1976 - May 2, 1977: Persulphate digestion (hot plate)
   May 2, 1977 - April 1, 1979: modified Indophenol Blue method (sodium nitroprusside catalyst, AAII system)
   April 1, 1979 - August 1979: hot plate method, colourimetry as previous method

3. Laboratory: Dorset Lab, Dorset, August 1979 - June 1, 1982

   Sampling:
   Container - 500 mL or 1 L nalgene, acid base bath, distilled water rinse
   Field Collection - 76 μ filter, triple rinse, refrigeration

   Analysis: Samples are digested in a sulphuric acid mercuric oxide potassium sulphate media using two block digesters kept at 200°C and 360°C. The pH of the digestate is adjusted in-line in two stages, and then ammonia is determined by formation of indophenol blue in a buffered system using nitroprusside as a catalyst. Approximate absorbance: 0.25 at the 1,000 μg/L as N level.

   Instrumentation: Block digesters (2). Basic automated modular continuous flow system plus 1 module: 37°C bath (7.7 mL delay). Colourimetric measurement is through a 5.0 cm light path at 630 nm.

   Reporting:
   Maximum significant figures: 3
   Minimum increment (W): 5
   Detection limit (T): 15

4. Laboratory: Dorset Lab, Dorset, June 1, 1982 - June 4, 1984

   Sampling:
   Container - 450 mL polystyrene with non-pulp lined cap
   Field Collection - 76 μ filter, triple rinse, refrigeration

   Analysis: Samples are digested in a sulphuric acid mercuric oxide potassium sulphate media using two block digesters kept at 200°C and 360°C. The pH of the digestate is adjusted in-line in two stages, and then ammonia is determined by formation of indophenol blue in a buffered system using nitroprusside as a catalyst. Approximate absorbance: 0.25 at the 1,000 μg/L as N level.

5. Laboratory: River and Lakes Lab, Toronto, June 4, 1984 - present (in mg/L as N)

   Sampling:
   Container - 450 mL polystyrene with non-pulp lined cap
   Field Collection - 76 μ filter, triple rinse, refrigeration

Table C17 (cont'd.)

Analysis	Samples are digested in a sulphuric acid mercuric oxide potassium sulphate media using two block digesters kept at 200°C and 360°C. The pH of the digestate is adjusted in-line in two stages, and then ammonia is determined by formation of indophenol blue in a buffered system using nitroprusside as a catalyst. Approximate absorbance: 0.25 at the 1,000 μg/L as N level.

APPENDIX D

Data Editing Procedures

INTRODUCTION

All water chemistry data collected by the Dorset Research Centre (DRC) including lakes, streams and precipitation are stored in an ORACLE relational database. This provides for easy update and retrieval, as well as ensuring database security and integrity.

The chemistry data are entered weekly to the Lab Information System (LIS). Weekly submissions to the Sample Information System (SIS) at the Downsview Computer Centre are completed from both the Dorset and Rexdale Laboratory Services Branch (LSB) labs. The chemical data are retrieved every second week by DRC staff from SIS to update the water chemistry database (called "WATER"). These data entry procedures are summarized in Locke (1990) and David (1992).

Data are accessed from ORACLE with Structured Query Language (SQL) commands which readily accesses the data in a speedy and documented manner (Lazerte 1989a).

A program called Q (Lazerte 1989b), developed for ORACLE and written in the programming language C, computes the theoretical parameters used to compare with observed values. Data editing of the water chemistry database are made on a regular basis for the lake, stream and precipitation data.

Sample location, dates, condition codes and description information is printed with each sample. This will yield information re contamination evident at the time of sampling. A series of theoretical parameter calculations, data print outs, data plots and regressions comprise the edit procedures necessary to ensure the quality of our database. A visual check of the data print outs and regression plots often allows identification of data values outside an accepted range for particular sites. Values may be cross-checked against other sites where similar values are expected, although local events may alter the chemistry of a site. Certain parameters exhibit seasonal variations or fluctuate with other parameters. For this reason, many parameters are plotted over the edit date range, often with multiple charts of covarying parameters on the same page. This procedure helps to identify outliers from seasonal and event fluctuations.

A basic principle of water chemistry involves charge balance relationships. Four separate charge balances are computed. Each successive charge balance calculation adds parameters to refine the charge balance estimate which isolates the parameter group responsible for the charge balance deviations. The charge balance parameters often will identify an entire sample that has been contaminated, and whose values must be discarded. Any changes made to the ORACLE database use well documented accepted database updating procedures (David 1992). A final edit check to verify any data corrections is completed by repeating the edit procedure.

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